

KINETICS OF THE ELECTRODE REACTIONS OF SOME METAL COMPLEX SYSTEMS AT AMALGAMS

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This dissertation summarizes the results from the following papers.
They will be referred to by their Roman numerals.

I. Fronæus, S. and Johansson, C.L.

The Mechanism of the Electrode Process between Copper
Amalgam and Copper Glycollate Solutions.

J. Electroanal. Chem., 48 (1973) 195.

II. Fronæus, S. and Johansson, C.L.

Kinetics of the Electrode Process between Copper Amalgam
and Copper(II) Glyoxylate and Puryvate Solutions.

J. Electroanal. Chem., 60 (1975) 29.

III. Fronæus, S. and Johansson, C.L.

Kinetics of the $\text{Zn(II)}/\text{Zn(Hg)}$ Electrode Reactions in DMSO
Solutions of Halide Ions.

J. Electroanal. Chem., 80 (1977) 283.

IV. Johansson, C.L.

Kinetics of the $\text{Cd(II)}/\text{Cd(Hg)}$ Electrode Reactions in DMSO
Solutions of Halide Ions.

Manuscript.

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1. INTRODUCTION

1.1 Background

From investigations of the kinetics of electrode reactions at mercury or liquid amalgams with participation of metal ions it has for a long time been known that different specifically adsorbed anions often have a significant rate enhancing influence, that cannot be accounted for solely as a Frumkin effect, i.e. a coulombic attraction of the reactant by the electrode double-layer field.

Heyrovsky¹ was the first to suggest that catalysis by halide ions at the reduction of different metal ions, e.g. Bi(III), Sb(III), and In(III), is due to electron transfer through a halide bridge between the electrode and the metal ion. However, only in a few cases, which have been thoroughly discussed by de Levie² in a review article, has it been possible to give convincing evidence that specifically adsorbed anions are involved in the electrode reactions. To these cases belong the investigations by Aikens and Ross³ on the influence of halide ions on the rate of oxidation of Cr(II) and similar measurements by Barclay et al.⁴ on the effect from the thiocyanate ion. There it could be proved by product analysis that specifically adsorbed anions functioned as ligand bridges. Another case is the polarographic investigation by Pospíšil and de Levie⁵ on the reduction of In(III) in the presence of thiocyanate ions. Here a direct evidence is not possible, but the authors were able to show that most probably the reaction mechanism involves ligand bridging.

For other electrode reactions at amalgams the explanations given of the rate enhancing effect by different complex forming anions are more uncertain. In the frequently studied zinc halide systems in water solutions the rate increasing effect runs parallel with the adsorbabilities, i. e. $\text{Cl}^- < \text{Br}^- < \text{I}^-$, but counter to the tendencies⁶ of these anions to form complexes with the hard acceptor Zn^{2+} . Most authors⁷⁻⁹ have concluded, that the rate enhancement in these systems is due to specific adsorption of halide ions, without mentioning explicitly ligand bridging as a possible mechanism, whereas others¹⁰ have ascribed the effect to formation of electroactive complexes.

Thus, when discussing electrocatalysis by anions, authors have very often emphasized the importance of specific adsorption on the electrode surface. However, it should be pointed out that for some systems it has been shown convincingly that the catalyzed charge transfer at the amalgam is controlled by a single complex, e.g. the complex BiCl_2^+ in the Bi(III) chloride¹¹ system, also in a ligand concentration range where the bulk concentration of this complex can be very low compared to that of the dominant metal complex in the solution. In such a case it does not seem reasonable to ascribe the rate enhancement solely to specific adsorption of the ligand, leading to ligand bridging, but most probably the effect then also depends on some other property of the reacting complex, making it more electroactive.

The aim of the present series of investigations, dealing with the

kinetics of the electrode reactions of some metal complex systems at amalgams, was to further elucidate the importance of different factors, connected with the complex formation, for the rate of the charge transfer.

1.2 Selection of complex systems and solvents

For the attainment of the goal set up for the investigations it is important that the following conditions about the selected systems are fulfilled. (a) The rate of the electrode reaction at the amalgam should be of a suitable height, so that it can be accurately measured with the techniques available. (b) The complex formation must not be very weak, if the participation of different complexes in the electrode reaction is to be studied. (c) The stability constants of the complexes formed must be known, so that the concentrations of the complexes in the measurement solutions can be calculated. Furthermore, it is favourable if also other thermodynamic quantities, related to the complex formation, are known. The two first-mentioned conditions can sometimes be met with by selecting a solvent where the solvations of the metal ion and the ligand are of suitable strength.

In a previous investigation¹² in this laboratory on the $\text{Cu(II)}/\text{Cu(Hg)}$ electrode reaction in acetate solutions with water as solvent it was found that the acetate ions have a pronounced catalytic effect on the charge transfer. For this reason it seemed very interesting to study the effect of some other carboxylate ions with different tendencies for chelating with copper(II). Thus, as ligands were selected the

glycollate, glyoxylate, and pyruvate ions, especially as in certain homogeneous redox reactions¹³ such ligands display varying abilities to function as electron conducting ligand bridges.

As mentioned above the thoroughly investigated acceleration effect of halide ions on the Zn(II)/Zn(Hg) electrode reaction in water solutions has not been unambiguously explained. The difficulty in determining whether ligand bridging is of importance for the charge transfer with these systems is partly due to the very weak complex formation. Thus, it seemed worthwhile to select another solvent, where the complex formation is stronger. The aprotic solvent dimethylsulfoxide (DMSO) has been chosen, as the stability constants of the zinc halide systems in this solvent have recently¹⁴ been determined in this laboratory and found to be much higher than in water solutions, especially with Cl^- and Br^- as ligands.

In the introduction of paper IV different opinions about the mechanism of the Cd(II)/Cd(Hg) electrode reaction in non-complex perchlorate solutions have been presented. A step-wise charge transfer has been suggested by several authors¹⁵⁻¹⁷, but in most cases a convincing evidence of a step-wise mechanism has not been obtained. For the cadmium chloride system in water solutions it is quite clear¹⁸ that the electrode reaction is catalyzed by Cl^- , but owing to the very high rate of reaction different measurement techniques have given varying results.¹⁹ Thus, it seemed important to investigate the electrode reactions of the halide systems in a solvent where a strong solvation of Cd(II) gives so low rates of reaction that accurate mea-

surements are made possible. DMSO proved to meet with this requirement. For this solvent the thermodynamic data of the complex formation in the Cd(II) halide systems are also known.²⁰ Furthermore, with the same choice of solvent for the studies of the zinc and cadmium systems the results obtained for the hard acceptor Zn^{2+} could be compared with those for the softer acceptor Cd^{2+} .

2. THEORETICAL

2.1 Equations for the exchange current density

According to measurements on the complex equilibria all of the systems in the present series of investigations consist of only mononuclear complexes at the low total concentrations of the central ions used in the kinetic measurements. Then, with the notations M^{2+} and L^- of the central ion and the ligand, respectively, eqn. (1) represents a set of possible, parallel overall electrode reactions. As usual the solvent ligands have been omitted for the sake of brevity.

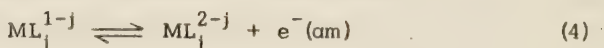
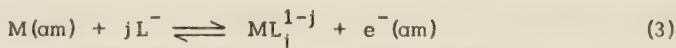


If it is presumed that these are simple one-step reactions, general theory for electrode kinetics gives the following expression for the total exchange current density (cf. refs. 12 and 21).

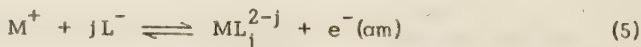
$$i_0 = \sum_j k_j [\text{M}^{2+}]^{\alpha_j} [\text{L}^-]^j \quad (0 < \alpha_j < 1) \quad (2)$$

Here α_j is the anodic transfer coefficient of reaction (1) and k_j is a composite coefficient for which the complete expression is given in III and IV. It contains the true rate constant k'_j , the stability constant β_j of the complex ML_j^{2-j} , the amalgam concentration, and the Frumkin correction for the influence of the ϕ_2 -potential. For a constant amalgam concentration k_j can be expected to be a constant, if a supporting electrolyte in high and constant concentration is used, so that variations in the activity coefficients and in the ϕ_2 -potential at varying but low $[L^-]$ can be presupposed to be suppressed.

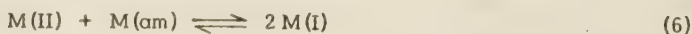
Another possibility, that sometimes seems more probable (cf. ref. 22), is that the overall electrode reactions (1) are not simple two-electron reactions but proceed step-wise with the solvated $M(I)$ as an intermediate.



If M^+ has no tendency to form complexes with L^- , eqn. (4) should be exchanged for the following one (cf. IV), and then eqn. (3) is valid only for $j=0$.



In the case of step-wise electrode reactions the disproportionation equilibrium is to be taken into consideration.



Then, as expressions for the current densities $i_{0,1}$ and $i_{0,2}$ of the steps (3) and (4) the following equations are obtained.

$$i_{0,1} = \sum_j k_{j,1} [M^{2+}]^{\alpha_{j,1}/2} [L^-]^j \quad (0 < \alpha_{j,1} < 1) \quad (7)$$

$$i_{0,2} = \sum_j k_{j,2} [M^{2+}]^{(1+\alpha_{j,2})/2} [L^-]^j \quad (0 < \alpha_{j,2} < 1) \quad (8)$$

$k_{j,1}$ and $k_{j,2}$ are composite coefficients for which the complete expressions are presented in IV. In addition to the true rate constants $k'_{j,1}$ and $k'_{j,2}$, Frumkin corrections, $[M(am)]$, and β_j (in case of $k_{j,2}$) they also contain the stability constant γ_j of ML_j^{1-j} and the equilibrium constant K for the equilibrium (6) applied to the free central ions. If these different constants are known it should in principle be possible to obtain the kinetic parameters, i.e. the rate constants and transfer coefficients, from determinations of $i_{0,1}$ and $i_{0,2}$. Very often step (4) is the rate-determining one and then for different complexes the constants $k'_{j,2}$ can be compared, since they all have the same dimension length/time.

If reaction (5) is applied instead of (4) the rate constants $k'_{j,2}$ retain the dimension mentioned, if the quantity $[\text{solvent}]^{-j}$ instead of γ_j is put into the expression for the composite coefficient $k_{j,2}$. These things are more fully treated in paper IV.

In paper I it is shown that the electrochemically determined i_0 can be composed of $i_{0,1}$ and $i_{0,2}$ in two different ways. If the non-electrochemical disproportionation (6) is slow compared with the charge transfer steps and the concentration of the intermediate

M(I) is very low, then at polarization a steady state with consecutive charge transfer steps should be obtained, for which the following relationship is valid.

$$i_0^{-1} = 0.5 (i_{0,1}^{-1} + i_{0,2}^{-1}) \quad (9)$$

On the other hand, if the disproportionation is much faster, then at small polarizations (3) and (4) can be treated as parallel single-electron steps, and for i_0 eqn. (10) should hold.

$$i_0 = 0.5 (i_{0,1} + i_{0,2}) \quad (10)$$

In both cases i_0 is calculated from the transfer resistance, R_t , (see below) according to the relation $R_t = RT/2FAi_0$, where A is the area of the polarizable electrode.

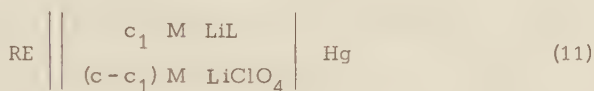
In the settling of the mechanism of the charge transfer, studies of a function¹² $\bar{\alpha} = (\partial \log i_0 / \partial \log [M^{2+}])_{[L^-]}$ have proved very useful. $\bar{\alpha}$ is a sort of average (cf. I) of the different exponents for $[M^{2+}]$ in the complete expression for i_0 . It is easily seen that quite different values of $\bar{\alpha}$ should be expected for $i_0 \sim i_{0,1}$ and $i_0 \sim i_{0,2}$. $\bar{\alpha}$ -values round about 0.25 and 0.75, respectively, are plausible in the two cases.

2.2 Specific anion adsorption and ϕ_2 -potentials

For the elucidation of the importance of ligand bridging for the rate of the charge transfer it is of course necessary to have at least a qualitative information about specific adsorption of the ligand.

Furthermore, in order to correct for the Frumkin effect and obtain true rate constants it is required to have quantitative values of the ϕ_2 -potential. Since the electrode reactions of the zinc and cadmium halide systems were studied in DMSO solutions (papers III and IV) and double-layer data for this solvent seemed to be available only in the case of the chloride ion²³, it was appropriate to carry out electrocapillary measurements.

In these measurements a cell with liquid junction of the following type was used.



Here the mercury electrode is an ideal polarized electrode and RE denotes a fixed reference electrode. Then, if the temperature, the pressure and the ratio c/c_1 are kept constant, and it is presupposed that variations in the activity coefficients and in the liquid junction potential with varying c can be neglected, eqn. (12) is valid (cf. ref. 24 and III).

$$-d\gamma = qdE + (qF^{-1} + 2\Gamma_+)RTd\ln c \quad (12)$$

γ is the interfacial tension, q the charge density on the mercury, E the applied potential of the mercury versus RE and Γ_+ the surface excess of Li^+ relative the DMSO. From the electrocapillary curve, $\gamma(E)_c$, (cf. III) the quantity q can be obtained by applying the Lippmann equation, $q = -(\partial\gamma/\partial E)_c$, and then Γ_+ from the relation-

ship.

$$\Gamma_+ = -(q/2) [(\partial E / \partial \ln c)_\gamma / RT + F^{-1}] \quad (q \neq 0) \quad (13)$$

Finally, from q and Γ_+ and on the plausible assumption that Li^+ is not specifically adsorbed, the ϕ_2 -potential and the quantity q_-^1 of specifically adsorbed anions can be calculated according to the Gouy-Chapman theory (cf. ref. 24). The use of eqn. (13) for the calculation of Γ_+ has the advantage that the capillary electrometer in the determination of $(\partial E / \partial \ln c)_\gamma$ is used only to indicate a constant γ -value, and no quantitative determinations of small differences in γ are necessary. On the other hand, the condition $q \neq 0$ for validity of eqn. (13) makes it difficult to obtain reliable values of especially q_-^1 , if the E -value to be used is fairly close to the electrocapillary maximum.

In the measurements in III and IV q and Γ_+ were determined for $c = 1 \text{ M}$, the ionic strength used in the kinetic measurements, and for a value of E within the range of the equilibrium potential of the amalgam in the complex solutions. The results obtained relate to pure mercury, but very probably they are applicable also to the dilute zinc and cadmium amalgams used.

3. EXPERIMENTAL METHODS

3.1 Measurements of the charge transfer resistance

In the determinations of the exchange current density the polarizable electrode was a stationary amalgam drop. The counter electrode was an amalgam pool, but in the measurements on the cadmium halide systems two drops of equal size were used to diminish the dissolution of cadmium from the amalgam^{IV}.

In the studies of the copper systems and in some of the measurements on the zinc chloride system^{III} the charge transfer resistance was obtained from electrode impedance measurements by using an a.c. bridge, described in an earlier paper¹¹ from this laboratory. The voltage applied across the cell was of an amplitude ≤ 5 mV. Then, if the electrode reaction is controlled by charge transfer and diffusion only, the faradaic impedance in the equivalent circuit (Fig. 1) of the cell is represented by the charge transfer resistance, R_t , and the diffusion impedance, W , a so-called Warburg impedance for which it holds^{25,26} that $W = \text{const.} (1-j)\nu^{-\frac{1}{2}}$, where j is the imaginary unit vector and ν the frequency. In this case the faradaic impedance is said to display a "Randles behaviour". The compensation for the cell resistance and the procedure for obtaining the faradaic impedance and R_t from the total cell impedance were the same as described before¹¹. Frequencies between 20 and 2000 Hz of the voltage applied were used.

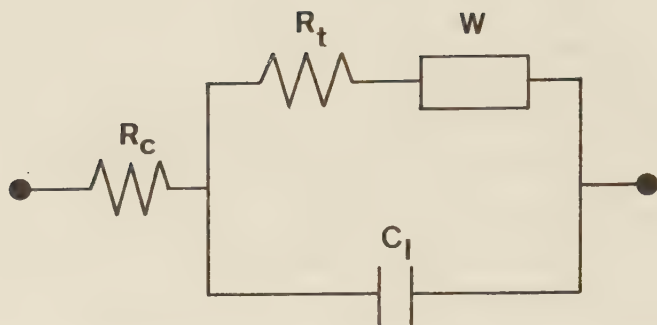


Fig. 1. Equivalent circuit of the cell. R_t , transfer resistance; W , Warburg impedance; C_l , double-layer capacitance; R_c , cell resistance.

Most of the measurements of i_0 in the zinc and cadmium halide systems in DMSO were performed according to a somewhat modified version of the cyclic current-step method²⁷. In this case the Wheatstone bridge was fed with a square-wave voltage and by using a suitable ratio^{III} between the frequencies of the sweep of the oscilloscope and of the square wave it was easy to determine the voltage response of the cell. The amplitude of this response was always kept < 10 mV and the frequencies of the square-wave < 100 Hz. Since at a time 0.09τ after the beginning of each half-period (duration $\tau/2$) the diffusion polarization is zero²⁷, it is evident from Fig. 1 that when the bridge is balanced at the time mentioned by adjusting a resistor, R_p , and a capacitor, C_p , in parallel, R_t is obtained directly from the R_p -value. When both the polarization methods were applied^{III} to the same solutions they gave consistent

R_t -values.

3.2 Electrocapillary measurements

The capillary electrometer was constructed according to models developed previously^{28,29}. The most important part of it was the tapering capillary, and in the measurements of both the interfacial tension and the surface excess, Γ_+ , it was essential to always bring the meniscus in the capillary to the same position. An Ag,AgCl electrode in a DMSO solution of constant $[Cl^-]$ was used as reference half-cell, and it functioned very well if $[Cl^-]$ was kept sufficiently low to prevent the silver chloride to be dissolved in DMSO as a result of formation of chloride complexes³⁰.

3.3 The ionic medium

To suppress variations in the activity constants and in the ϕ_2^- potential at varying ligand concentrations a constant ionic strength of 1 M was used throughout the kinetic measurements. To be able to use the stability constants previously determined^{14,20,31} it was necessary to keep to the same ionic media. Thus, for the copper carboxylate systems sodium perchlorate was used, while for the zinc and cadmium halide systems in DMSO ammonium perchlorate was the supporting electrolyte, though there is an indication³² that NH_4^+ in DMSO interacts with Cl^- via hydrogen bonds. As stability constants were not involved in the electrocapillary measurements lithium perchlorate was used as a very suitable supporting electro-

lyte in this case.

All measurements were performed at $25.0 \pm 0.2^{\circ}\text{C}$. The complex solutions were kept free from oxygen by a stream of pure nitrogen

4. RESULTS AND DISCUSSION

4.1 The copper(II) carboxylate systems

The electrode reactions of the copper(II) glycollate, glyoxylate and puryvate systems in water solutions have been treated in papers I and II, and the results obtained can be compared with those arrived at for the corresponding acetate system in a previous paper¹².

For all of these systems it was found by impedance measurements that they displayed a "Randles behaviour". Such a behaviour proves³³ that a possible specific adsorption of electroactive copper species on the amalgam surface must be weak and have such a high exchange adsorption rate that the electrode reaction is controlled solely by charge transfer and diffusion. Thus, the impedance measurements should give true i_0 -values.

The influence of the different carboxylate ligands on i_0 and $\bar{\alpha}$ at a constant copper concentration in the solutions is shown in Figs. 2 and 3, respectively. i_0 increases rapidly at increasing values of $[\text{L}^-]$, but in the glycollate system i_0 finally attains an approximately constant value at higher ligand concentrations. The quantity

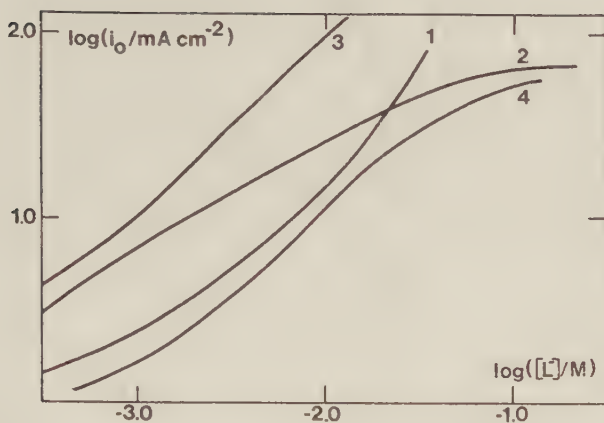


Fig. 2. The exchange current density as a function of the ligand concentration for the copper carboxylate systems.

$C_{\text{Cu(II)}} = 0.66 \text{ mM}$. L^- : (1) CH_3COO^- ; (2) $\text{HOCH}_2\text{COO}^-$; (3) HCOCOO^- ; (4) $\text{CH}_3\text{COCOO}^-$.

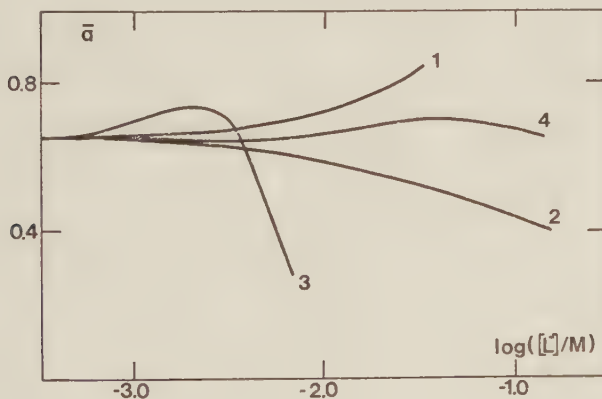


Fig. 3. $\bar{a}$ as a function of the ligand concentration for the copper carboxylate systems. $C_{\text{Cu(II)}} = 0.66 \text{ mM}$. The numbers of the curves refer to the same ligands as in Fig. 2.

$\bar{\alpha}$ has a value of about 0.7 at low $[L^-]$ in all of the four systems, but the variation in $\bar{\alpha}$ at increasing $[L^-]$ is very different.

The measurements on the acetate system alone¹² did not permit a distinction to be made between two possible charge transfer mechanisms, either two-electron transfers or one-electron steps according to reactions (3) and (4) with the step $\text{Cu(II)}/\text{Cu(I)}$ as rate-determining. However, in paper I it has been shown that the increase in i_0 and the simultaneous decrease in $\bar{\alpha}$ found in the glycollate system cannot be explained on the basis of eqn. (2). Thus, it was concluded that the overall electrode reactions (1) predominantly proceed as successive one-electron steps. Very probably this conclusion is valid also for the other carboxylate systems investigated.

Then, the high values of $\bar{\alpha}$ found throughout at very low ligand concentrations make it plausible that the step $\text{Cu(II)}/\text{Cu(I)}$ is the rate-determining one and consequently $i_0 \sim i_{0,2}$ in this range of $[L^-]$. The rapid increase in i_0 at increasing $[L^-]$ is then to be correlated with the formation of Cu(II) carboxylate complexes. The considerable decrease in $\bar{\alpha}$ at increasing glycollate concentrations indicates that the step $\text{Cu(I)}/\text{Cu(am)}$ is becoming rate-controlling, and i_0 is more influenced by the value of $i_{0,1}$. The stability of Cu(I) glycollate complexes can be expected to be very weak, as is the case with Ag(I) glycollate complexes³⁴, and thus the ratio $[\text{Cu(I)}]/[\text{Cu(II)}]$ should decrease with increasing $[L^-]$. This effect can explain the approximately constant i_0 found at the highest glycollate concentrations. It is easily seen that the results obtained

KINETICS OF THE $\text{Cd(II)}/\text{Cd(Hg)}$ ELECTRODE REACTIONS IN DMSO
SOLUTIONS OF HALIDE IONS

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ABSTRACT

The electrode reaction Cd(II)/Cd(Hg) in complex chloride, bromide and iodide solutions with dimethylsulfoxide as solvent has been studied by a cyclic current-step method. The ionic strength was 1 M with ammonium perchlorate as supporting electrolyte. The ϕ_2 -potential of the double-layer has been determined by electrocapillary measurements. The results indicate that the overall charge transfer proceeds step-wise and is accompanied by a fast disproportionation of the intermediate Cd(I) . In the chloride system it is not possible to detect that the complexes formed take part in the electrode reaction, while in the bromide and iodide systems Cd^{2+} as well as the complexes CdX^+ and CdX_2 contribute to the exchange current density. It is suggested that the rate constant of the step $\text{CdX}_j^{2-j}/\text{Cd(I)}$ depends on the possibility of ligand bridging at the amalgam by X^- and on the total enthalpy change at the formation of CdX_j^{2-j} from the solvated Cd^{2+} .

INTRODUCTION

For the Cd(II)/Cd(Hg) electrode reaction in water solutions of NaClO_4 Barker [1] found an unusually low value of the cathodic transfer coefficient. To account for this, Bockris [2] suggested a step-wise reaction with Cd^+ as an intermediate, and Lovrec ek and Marin ci  [3] proposed in addition a fast disproportionation of Cd^+ . Biegler et.al. [4] have studied this reaction in water as well as in various non-aqueous solvents and throughout found low values of the cathodic transfer

coefficient. They discussed Cd_2^{2+} as a possible intermediate but concluded that a transition state with a partially discharged and specifically adsorbed Cd^{2+} gives the most probable mechanism.

In water solutions of KCl different experimental methods give inconsistent results (cf. ref. 5), probably because of the high rate of reaction. In a recent investigation van der Pol et al. [6] suggested that the rate-determining step is chemical instead of electrochemical, but no definite conclusions could be drawn. However, it is quite clear that the reaction is accelerated by chloride ions.

In the present investigation dimethylsulfoxide (DMSO) was chosen as solvent as from the results of an earlier investigation [7] on the electrode reactions of the zinc halide systems in DMSO it could be expected that the rate of the charge transfer in the cadmium systems would be lower in DMSO than in water and make an accurate determination of the exchange current density possible. The suggestion [7] that in DMSO the larger solvent molecules form a steric hindrance to ligand bridging between the metal ion and the electrode by Cl^- or Br^- could also be tested. The stability constants of the cadmium halide systems, necessary for our calculations, have recently been determined by Ahrlund and Björk [8].

To be able to apply a Frumkin correction to the rate constants electrocapillary measurements for the determination of values of the ϕ_2 -potential have also been carried out.

EXPERIMENTAL

Chemicals

$\text{Cd}(\text{DMSO})_6(\text{ClO}_4)_2$ was prepared from cadmium perchlorate hexahydrate and purified DMSO according to Ahrlund and Björk [9]. Titration with EDTA showed that the salt had the correct molecular weight. Liquid cadmium amalgam, 0.1 % by weight, was prepared by adding analytical grade cadmium powder to mercury, covered by diluted perchloric acid and kept at 70 °C. The amalgam was formed immediately and was washed with deaerated water and kept in a nitrogen atmosphere. This amalgam was used in all the kinetic measurements. Analytical grade ammonium and lithium perchlorates, chlorides, bromides and ammonium iodide were dried at 110 °C before using. Lithium iodide was used directly.

Experimental details

In the measurements of the electrode kinetics an amalgam pool could not be used as counter electrode, because of some dissolution of cadmium into the DMSO solution. Instead both electrodes were stationary amalgam drops. New drops were applied before each measurement. The surface area of a single drop was 0.034 cm^2 and the distance between the electrodes was 1.8 cm.

The cyclic current step method of Wijnen and Smit [10] was used in all the kinetic measurements. The modification of the method and the electronic equipment were the same as in the investigation of the zinc systems [7]. The current was adjusted so that the voltage across the cell was kept smaller

than 10 mV. Stable and reproducible values of R_t were obtained almost immediately after renewing of the amalgam drops. In the electrocapillary measurements the capillary electrometer and other experimental equipment used were the same as in the previous investigation [7].

All measurements were performed at 25.0 ± 0.2 °C. The complex solutions were de-aerated by a stream of oxygen-free nitrogen. The ionic strength of the solutions was 1 M with ammonium perchlorate as supporting electrolyte in the kinetic measurements. To avoid an interaction [11] between NH_4^+ and the halide ions via hydrogen bonds, a lithium perchlorate medium was used in the electrocapillary measurements.

THEORETICAL

List of symbols

i_0	the electrochemically determined exchange current density of the overall reaction $\text{Cd(am)} \rightleftharpoons \text{Cd(II)} + 2e^-$
$i_{0,1}; i_{0,2}$	exchange current densities of the steps $\text{Cd(I)}/\text{Cd(am)}$ and $\text{Cd(II)}/\text{Cd(I)}$
$k_j'; \alpha_j$	the true rate constant and the anodic transfer coefficient of the reaction $\text{CdX}_j^{2-j}/\text{Cd(am)}$
$k_{j,1}'; \alpha_{j,1}$ $k_{j,2}'; \alpha_{j,2}$	true rate constants and anodic transfer coefficients of the steps $\text{CdX}_j^{1-j}/\text{Cd(am)}$ and $\text{CdX}_j^{2-j}/\text{CdX}_j^{1-j}$
β_j, γ_j	
K	stability constants of CdX_j^{2-j} and CdX_j^{1-j}
	equilibrium constant of $\text{Cd}^{2+} + \text{Cd(am)} \rightleftharpoons 2\text{Cd}^+$
k_j	$= 2Fk_j'\beta_j^{\alpha_j} \exp\{(j-2\alpha_j)F\phi_2/RT\} [\text{Cd(am)}]^{1-\alpha_j}$

$$k_{j,1} = Fk_{j,1}' \gamma_j^{\alpha_{j,1}} K_{j,1}^{\alpha_{j,1}/2} \exp\{(j-\alpha_{j,1})F\phi_2/RT\} [Cd(am)]^{1-\alpha_{j,1}/2}$$

$$k_{j,2} = Fk_{j,2}' \gamma_j^{1-\alpha_{j,2}} \beta_j^{\alpha_{j,2}} K_{j,2}^{(1-\alpha_{j,2})/2} \exp\{(j-1-\alpha_{j,2})F\phi_2/RT\} [Cd(am)]^{(1-\alpha_{j,2})/2}$$

$$\bar{\alpha} = (\partial \log i_0 / \partial \log [Cd^{2+}]) [X^-]$$

The exponential factors represent the Frumkin correction for the influence of the ϕ_2 -potential.

Equations for the exchange current density

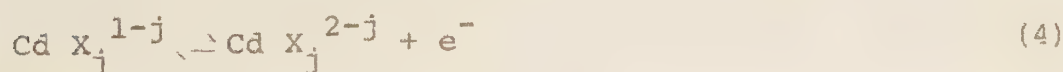
According to Ahrland and Björk [8] Cd^{2+} forms mononuclear complexes with the halide ions in DMSO. Then, for the overall charge transfer reaction, we have to consider a set of parallel reactions ($X^- = Cl^-, Br^-$ or I^-)



If these are single-step reactions, the expressions for the overall exchange current density will be (cf. ref. 12)

$$i_0 = \sum_j k_j [Cd^{2+}]^{\alpha_j} [X^-]^j \quad (0 < \alpha_j < 1) \quad (2)$$

On the other hand, the overall charge transfer processes (1) could also proceed step-wise according to the scheme



For the current densities $i_{0,1}$ and $i_{0,2}$ one obtains the expressions [12]

$$i_{0,1} = \sum_j k_{j,1} [\text{Cd}^{2+}]^{\alpha_{j,1}/2} [\text{X}^-]^j \quad (0 < \alpha_{j,1}/2 < 0.5) \quad (5)$$

$$i_{0,2} = \sum_j k_{j,2} [\text{Cd}^{2+}]^{(1+\alpha_{j,2})/2} [\text{X}^-]^j \quad (0.5 < (1+\alpha_{j,2})/2 < 1) \quad (6)$$

Values of $\bar{\alpha}$ of about 0.25 should be expected if $i_0 \sim i_{0,1}$ and of about 0.75 if $i_0 \sim i_{0,2}$.

In two previous papers [13,14] where similar equations were derived for copper systems, it was shown that if the disproportionation reaction, in this case $\text{Cd(am)} + \text{Cd(II)} \rightleftharpoons 2 \text{Cd(I)}$, is slow in comparison with the charge transfer steps and the concentration of the intermediate is very low, the electrochemically determined i_0 will be composed of $i_{0,1}$ and $i_{0,2}$ according to the expression

$$i_0^{-1} = 0.5(i_{0,1}^{-1} + i_{0,2}^{-1}) \quad (7)$$

On the other hand, if the disproportionation is much faster, then at small polarizations the Cd(I) concentration does not change. We then have two parallel single-electron steps and for the electrochemically determined i_0 eq. (8) should be valid.

$$i_0 = 0.5(i_{0,1} + i_{0,2}) \quad (8)$$

In the derivation it has been presupposed that i_0 in both cases is calculated in the same way [12] from R_t .

Measurements and calculations

In the main measurement series (Table 1) on the chloride system the total cadmium(II) concentration, C_{Cd} , was kept constant while C_{Cl} was varied. Since i_0 decreases monotonically on addition of chloride ions it was necessary to keep $C_{\text{Cl}} < 40 \text{ mM}$ to obtain reliable R_t -values. From the stability constants [8] $\beta_1 = 1700 \text{ M}^{-1}$, $\beta_2 = 1.5 \times 10^5 \text{ M}^{-2}$, $\beta_3 = 6.0 \times 10^7 \text{ M}^{-3}$ and $\beta_4 = 3.5 \times 10^9 \text{ M}^{-4}$ $[\text{Cd}^{2+}]$ and $[\text{Cl}^-]$ were calculated as described for zinc systems in a preceding paper [7].

In the other measurement series at constant $[\text{Cl}^-]$, aiming at determinations of $\bar{\alpha}$, $[\text{Cd}^{2+}]$ and the relationship between C_{Cd} and C_{Cl} were calculated by means of the constants.

From Fig. 1 it is obvious that all the measurements, including those on pure perchlorate solutions, can be represented fairly well by a single $(\log i_0, \log[\text{Cd}^{2+}])$ -curve. Thus, i_0 is a function of $[\text{Cd}^{2+}]$ exclusively, and the from eqns. (2), (5) and (6) it is clear that at the $[\text{Cl}^-]$ -values used the solvated cadmium ions completely predominate the charge transfer, though in some of the solutions $[\text{Cd}^{2+}]$ is but a small fraction of C_{Cd} (Table 1).

Since $(\partial i_0 / \partial [\text{Cl}^-])_{[\text{Cd}^{2+}]} = 0$ in this system, $\bar{\alpha}$ should be equal to the slope of the experimental curve. Then, at the highest $[\text{Cd}^{2+}]$ -values used $\bar{\alpha} = 0.80 \pm 0.02$ is obtained, while the lowest ones give $\bar{\alpha} = 0.25 \pm 0.02$. From this result the important conclusion that the charge transfer cannot predominantly be a simple one-step, two-electron reaction but most probably proceeds as successive single-electron steps can be drawn. The values of $\bar{\alpha}$ found make it plausible that as an

approximation $i_0 \sim i_{0,2}$ at high $[\text{Cd}^{2+}]$ and $i_0 \sim i_{0,1}$ at low $[\text{Cd}^{2+}]$. It is easily seen that this conclusion implies that eqn. (8) is applicable whereas eqn. (7) is not.

Then, since chloride complexes do not take part noticeably in the electrode reaction the expression (9) should be valid

$$i_0 = 0.5(k_{0,1}[\text{Cd}^{2+}]^{\alpha_{0,1}/2} + k_{0,2}[\text{Cd}^{2+}]^{(1+\alpha_{0,2})/2}) \quad (9)$$

Differentiation of eqn. (8) yields

$$4 i_0 \bar{\alpha} = i_{0,1} \alpha_{0,1} + i_{0,2} (1 + \alpha_{0,2}) \quad (10)$$

By drawing linear asymptotes to the curve in Fig. 1 one finds $i_{0,1} \approx 0.1 i_{0,2}$ at the highest $[\text{Cd}^{2+}]$ used and $i_{0,1} \approx 10 i_{0,2}$ at the lowest $[\text{Cd}^{2+}]$. Then, inserting the corresponding $\bar{\alpha}$ -values in eqn. (10) the exponents $\alpha_{0,1}/2 = 0.20 \pm 0.02$ and $(1+\alpha_{0,2})/2 = 0.85 \pm 0.2$ in the expression for i_0 is obtained. Finally, adjusting the coefficients $k_{0,1}$ and $k_{0,2}$ to the best fit with the measurements the values given in Table 4 is received. From the reproducibility of the i_0 -values at different $[\text{Cl}^-]$ an estimation of the upper limits of the coefficients $k_{1,2}$ and $k_{2,2}$ that are consistent with an undetectable contribution from CdCl^+ and CdCl_2 to i_0 can also be made.

The dimeric Cd_2^{2+} has been suggested [4] as a possible intermediate in water solutions. Then at high $[\text{Cd}^{2+}]$ a slope > 1 should be found for the $(\log i_0, \log[\text{Cd}^{2+}])$ -curve, and for this reason such an intermediate is improbable in the present case.

For the bromide system the measurements are collected in Table 2. The stability constants [8] used in the calculations are $\beta_1 = 830 \text{ M}^{-1}$, $\beta_2 = 7.0 \times 10^4 \text{ M}^{-2}$, $\beta_3 = 3.8 \times 10^7 \text{ M}^{-3}$ and $\beta_4 = 1.8 \times 10^9 \text{ M}^{-4}$. Also in this system i_0 decreases monotonically at a constant C_{Cd} and increasing C_{Br} . However, from the plot in Fig. 2 it is evident that i_0 is not a function of $[\text{Cd}^{2+}]$ exclusively but depends also upon $[\text{Br}^-]$. Combining eqns. (5), (6) and (8) and presupposing that the exponents for $[\text{Cd}^{2+}]$ are the same as in the chloride system one should expect plots of $i_0/[\text{Cd}^{2+}]^{0.20}$ versus $[\text{Cd}^{2+}]^{0.65}$ at the different constant $[\text{Br}^-]$ to be straight lines. This is also found, and furthermore $i_{0,1}$ can also in this system be represented by a single term $k_{0,1}[\text{Cd}^{2+}]^{0.20}$. Then from the function $(i_0 - 0.5 k_{0,1}[\text{Cd}^{2+}]^{0.20})/[\text{Cd}^{2+}]^{0.85}$, which should be a polynomial in $[\text{Br}^-]$, the coefficients $k_{j,2}$ have been determined (Table 4). From Fig. 2 it is seen that the i_0 -function calculated by use of the coefficients determined represents the measurement data very well. Only at the lowest C_{Cd} -values is the measured i_0 somewhat higher than the calculated one. The reason is a small dissolution of cadmium from the amalgam.

From the results it can be concluded that bromide complexes of Cd(I) do not detectably take part in the step Cd(I)/Cd(am), while besides the solvated Cd^{2+} most probably both CdBr^+ and especially CdBr_2 take part in the other step, Cd(II)/Cd(I). As a consequence $i_{0,2} > i_{0,1}$ in the whole measurement range.

The measurements on the iodide system are given in Table 3. The stability constants [8] used are in this case $\beta_1 = 150 \text{ M}^{-1}$, $\beta_2 = 4.0 \times 10^3 \text{ M}^{-2}$, $\beta_3 = 3.2 \times 10^6 \text{ M}^{-3}$ and $\beta_4 = 4.5 \times 10^7 \text{ M}^{-4}$.

From Fig. 3 it is seen that i_0 is a function of both $[\text{Cd}^{2+}]$ and $[\text{I}^-]$. The measurement series at different constant $[\text{I}^-]$ indicate that $\bar{\alpha} \approx 0.85$, independent of the $[\text{I}^-]$ -value. From this it is evident that in eqn. (8) the term $i_{0,1}$ is negligible in this system, and that in the expression (6) for $i_{0,2}$ all the exponents for $[\text{Cd}^{2+}]$ can be put equal to 0.85. Then, the coefficients $k_{j,2}$ can easily be computed (Table 4) from the function $i_0/[\text{Cd}^{2+}]^{0.85}$. Also in this case it is found (Fig. 3) that the coefficients determined give an i_0 -function that represents the measurement data very well.

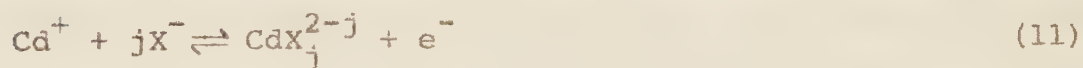
According to the calculations the complexes CdI^+ and CdI_2 give so large contributions to i_0 ($\approx i_{0,2}$) that at a constant C_{Cd} there is a pronounced catalysis of the charge transfer on addition of iodide ions. Only at larger $[\text{I}^-]$, when higher, anionic complexes are formed in the bulk of the solution, does i_0 decrease again.

The ϕ_2 -potentials and the true rate constants

The ϕ_2 -potentials were determined from electrocapillary measurements on pure mercury in contact with 1 M mixtures of lithium perchlorate and lithium halide in DMSO. The charge density, q , on the mercury at an applied potential, E , versus a fixed reference electrode (see Table 5) was obtained from the slope of the electrocapillary curves in the preceding paper [7]. The selected potential, $E = -785$ mV, corresponds approximately to the equilibrium potential of the cadmium amalgam in a solution with $C_{\text{Cd}} = 2$ mM and $[\text{Br}^-] = 10$ mM or $[\text{I}^-] = 25$ mM. The relative surface excess Γ_+ was determined as described

before [7] and, on the assumption that lithium ions are not specifically adsorbed, the ϕ_2 -potential was calculated according to the Gouy-Chapman theory (cf. ref. 15). From Table 5 it is evident that ϕ_2 varies only slightly with the different electrolyte mixtures, and the value obtained with 1 M LiCl is in agreement with that given by Kim et al. [16] at the same q -value. For the calculation of the exponential factor, the Frumkin correction, in the expressions for k_j , $k_{j,1}$ and $k_{j,2}$ the average value $\phi_2 = -40$ mV was used.

In order to obtain values of the ratios $k'_{1,2}/k'_{0,2}$ and $k'_{2,2}/k'_{1,2}$ it is necessary to make some approximations about the unknown factors $\gamma_j^{1-\alpha_{j,2}}$. Since the exponent is as small as 0.30, and it can be presupposed that the values of γ_j are low, it would probably be justified to make the approximation $(\gamma_j/M^{-j})^{1-\alpha_{j,2}} \approx 1$. However, as there is no indication from the kinetic measurements - not even in the bromide system - that complexes of Cd(I) take part in the charge transfer step (Cd(I)/Cd(am), the step Cd(II)/Cd(I) could be re-formulated as



instead of the processes (4). Furthermore, as of course DMSO molecules are also involved in the electrode reactions, the rate constants should be functions of [DMSO]. Then, with the re-formulation of the step Cd(II)/Cd(I), it is appropriate to separate a factor $[\text{DMSO}]^{j(\alpha_{j,2}-1)}$ from the rate constant. Consequently, in the expression for the composite coefficients

$k_{j,2}$ given above, $\gamma_j^{1-\alpha_{j,2}}$ have to be exchanged for the factor mentioned, and then all the rate constants $k'_{j,2}$ retain the dimension length/time. Putting $[\text{DMSO}] = 14 \text{ M}$ the ratios of the true rate constants (Table 6) are computed. It should be pointed out that the values of these ratios obtained depend only by a constant factor of 2.2 on the choice of approximation. Such a factor has no influence on the conclusions that can be drawn from the measurements.

DISCUSSION

An apparent rate constant for the overall electrode reaction (1) of the solvated Cd^{2+} , valid in the range $0.3 \text{ mM} < [\text{Cd}^{2+}] < 6 \text{ mM}$, can be calculated by applying eqn. (2) to the uppermost part of the curve in Fig. 1. Then, using the expression for k_0 with $[\text{Cd(am)}] = 0.12 \text{ M}$ and the apparent anodic transfer coefficient $\alpha_0 = 0.80$, $k'_0 = (7.0 \pm 0.5) \times 10^{-4} \text{ cm s}^{-1}$ is obtained. If the Frumkin correction is not applied the value is about $9 \times 10^{-3} \text{ cm s}^{-1}$. In water solutions with $1.0 - 0.9 \text{ M NaClO}_4$ as supporting electrolyte an uncorrected apparent rate constant of 0.45 cm s^{-1} has been found [1,4]. Thus, the relative decrease in the rate constant, when exchanging water for DMSO as solvent, is of about the same magnitude for Cd^{2+} and Zn^{2+} [7]. This finding could be related to the not very different values [17], -68 and -60 kJ mol^{-1} , of the enthalpies of transfer of these ions from water to DMSO.

The very low value 0.20 of the apparent cathodic transfer coefficient, $1 - \alpha_0$, in the $[\text{Cd}^{2+}]$ -range mentioned above corresponds fairly well to values previously found [4] for

Cd^{2+} in perchlorate solutions in water and various non-aqueous solvents. This result could indicate one and the same mechanism of the charge transfer. Now, owing to the interesting fact that in DMSO cadmium chloride complexes do not contribute detectably to i_0 , it has been possible to study the electrode reaction of the solvated Cd^{2+} down to $[\text{Cd}^{2+}] \approx 10^{-7}$ M. The pronounced decrease in α_0 from 0.80 to 0.25 at decreasing $[\text{Cd}^{2+}]$, which can be completely explained on the basis of eqns. (5), (6) and (8), makes it most likely that the overall charge transfer proceeds step-wise with Cd^+ as an intermediate and furthermore is accompanied by a fast disproportionation. The mechanism arrived at gives constant and reasonable anodic transfer coefficients, $\alpha_{0,1} = 0.40$ and $\alpha_{0,2} = 0.70$, of the steps $\text{Cd}^+/\text{Cd(am)}$ and $\text{Cd}^{2+}/\text{Cd}^+$, respectively. This mechanism is similar to that proposed by Lovreček and Marinčić [3] for water solution.

Objections previously raised [4] to a mechanism involving Cd^+ in solution were based on the estimate [18] $1.9 \text{ V} < -E^\circ < 2.5 \text{ V}$ of the standard potential of the $\text{Cd}^{2+}/\text{Cd}^+$ couple in water solutions. However, if in the calculation of E° the valuation [18] of the free energy of hydration of Cd^+ by interpolation from the values [19] for the alkali metal ions is based on the use of the internally consistent crystallographic ionic radii of Morris [20] and Shannon and Prewitt [21] instead of the Pauling ionic radii, we obtain $1.0 \text{ V} < -E^\circ < 1.7 \text{ V}$. The free energy of hydration of Ag^+ [19] can also be used as a reasonable approximation, as Cd^+ and Ag^+ should have not very different radii. This approximation gives $E^\circ \approx -1.1 \text{ V}$. Using the last-mentioned value $K \approx 10^{-24}$ is calculated for water

solutions. With DMSO solutions it can be estimated that K is higher by a factor of about 10^6 , as is the case with the corresponding disproportionation of copper(I) (cf. refs. 13 and 22). Then, from the expressions for $k_{0,1}$ and $k_{0,2}$ one obtains $k'_{0,1} \approx k'_{0,2} \approx 1 \text{ cm s}^{-1}$. The result that the two steps of the electrode reaction of the non-complexed Cd^{2+} probably have rate constants of the same order of magnitude is fairly independent of the K -value, as is easily seen from the expressions used.

Thus, a mechanism with the intermediate Cd^+ in solution does not seem to give unreasonably high rate constants. On the other hand, the fast disproportionation, the existence of which is apparent from the measurements, is difficult to explain in terms of a bimolecular reaction in solution because of the very low equilibrium values of $[\text{Cd}^+]$ estimated. Thus, it must be concluded that weakly solvated Cd^+ is specifically adsorbed on the amalgam (cf. ref 4) and that a fast disproportionation of adsorbed Cd^+ takes place.

The finding that in DMSO chloride complexes of Cd(II) do not contribute detectably to i_0 , whereas in water solution the charge transfer is enhanced by the presence of Cl^- , can be accounted for in the same way as for the zinc chloride system [7]. In DMSO the solvent molecules probably make the distance between the amalgam surface and the central ion of the Cd(II) complexes in the pre-electrode layer too large to permit Cl^- to function as a ligand bridge. Then, no catalysis of the charge transfer can be expected, compensating for the Frumkin effect.

For the other larger halide ligands the steric hindrance should decrease in the order $\text{Br}^- > \text{I}^-$. The values of $k'_{1,2}/k'_{0,2}$ in Table 6 lead to the conclusion that ligand bridging is not very probable in the bromide system but could explain the pronounced catalysis of the charge transfer by the large I^- . The fact that $k'_{2,2}/k'_{1,2}$ has fairly similar values in the two systems makes it improbable that on coordination of a second I^- a double ligand bridge to the amalgam can be formed.

In previous measurements [7] on the zinc iodide system it was found that the charge transfer was promoted by the first complex, but the effect was not as pronounced as in the cadmium iodide system. Now, since Cd^{2+} is a softer acceptor than Zn^{2+} , the partial covalent character of the bond to I^- is larger, and for this reason the catalytic effect of ligand bridging should also be larger. Thus, the prediction is in agreement with the results obtained.

The large increase in the rate constant on the formation of CdBr_2 and CdI_2 could be correlated to the quite large and positive values (Table 6) of the enthalpy change, ΔH_2^0 , in the second step of the complex formation in DMSO. These positive ΔH_2^0 (and ΔS_2^0) have been interpreted [8] as due to a change from octahedral to tetrahedral coordination at this step. Such a change in the inner sphere solvation of CdX_2 should diminish the difference in solvation of Cd(II) and Cd(I) and consequently also lower the energy of activation of the corresponding charge transfer step. Preliminary measurements in this laboratory on the cadmium thiocyanate system [23] in DMSO have shown that in this case $k'_{1,2}/k'_{0,2}$ is somewhat higher than in the bromide

system, whereas $k'_{2,2}/k'_{1,2}$ is only about 1.5. Furthermore, $\Delta H_1^0 \approx \Delta H_2^0 \approx -3 \text{ kJ mol}^{-1}$ in the thiocyanate system [8]. The results above taken together support the suggestion that the rate constant of the step $\text{CdX}_j^{2-j}/\text{Cd(I)}$ depends on both the possibility of ligand bridging at the amalgam and the total enthalpy change $\sum_{n=1}^j \Delta H_n^0$, at the formation of CdX_j^{2-j} .

Finally, it should be pointed out that for the third and fourth complexes, which predominate in the bulk of the solutions at the highest halide ion concentrations used, no additional rate enhancing effect can be anticipated. Then, at the negative ϕ_2 -potential calculated, the Frumkin effect aids in making the participation of these anionic complexes not observable in the electrode reaction.

ACKNOWLEDGEMENTS

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REFERENCES

1. G.C. Barker in E. Yeager (Ed.), Trans. Symp. Electrode Processes, Philadelphia 1959, Wiley, New York, 1961, p. 325.
2. J.O'M. Bockris in E. Yeager (Ed.), Trans. Symp. Electrode Processes, Philadelphia 1959, Wiley, New York, 1961, p. 325.
3. B. Lovreček and N. Marinčić, Electrochim. Acta, 11 (1966) 237.
4. T. Biegler, E.R. Gonzalez and R. Parsons, Collect. Czech. Chem. Commun., 36 (1971) 414.
5. H.P. van Leeuwen and J.H. Sluyters, J. Electroanal. Chem., 39 (1972) 233.
6. F. van der Pol, M. Sluyters-Rehbach and J.H. Sluyters, J. Electroanal. Chem., 58 (1975) 177.
7. S. Fronæus and C.L. Johansson, J. Electroanal. Chem., 80 (1977) 283.
8. S. Ahrland and N.O. Björk, Acta Chem. Scand., A 30 (1976) 249, 257.
9. S. Ahrland and N.O. Björk, Acta Chem. Scand., A 28 (1974) 823.
10. M.D. Wijnen and W.M. Smit, Rec. Trav. Chim., 79 (1960) 22, 203.
11. S. Ahrland and N.O. Björk, Coord. Chem. Rev., 16 (1975) 115.
12. S. Fronæus, R. Johansson and C.O. Östman, Chem. Scr., 1 (1971) 52.
13. S. Fronæus and C.L. Johansson, J. Electroanal. Chem., 48 (1973) 195.
14. S. Fronæus and C.L. Johansson, J. Electroanal. Chem., 60 (1975) 29.

15. Delahay, Double Layer and Electrode Kinetics, Interscience, New York, 1965.
16. S.H. Kim, T.N. Andersen and H. Eyring, J. Phys. Chem., 74 (1970) 4555.
17. S. Ahrland, L. Kullberg and R. Portanova, Acta Chem. Scand., A. To be published.
18. J.H. Baxendale and R.S. Dixon, Z. Phys. Chem. (Frankfurt), 43 (1964) 161.
19. R.M. Noyes, J. Am. Chem. Soc., 84 (1962) 513.
20. D.F.C. Morris in Structure and Bonding, Volume 4, Springer, Berlin, 1968, p. 63.
21. R.D. Shannon and C.T. Prewitt, Acta Crystallogr., B 25 (1969) 925.
22. A. Foll, M. Le Démezet and J. Courtot-Coupez, J. Electroanal. Chem., 35 (1972) 41.
23. S. Fronæus and B. Palm. To be published.

Fig. 1. $\log i_0$ as a function of $\log [\text{Cd}^{2+}]$ in the chloride system at a constant C_{Cd} or $[\text{Cl}^-]$. The symbols refer to the values given in Table 1. The curve has been calculated from the values of $k_{0,1}$ and $k_{0,2}$ in Table 4.

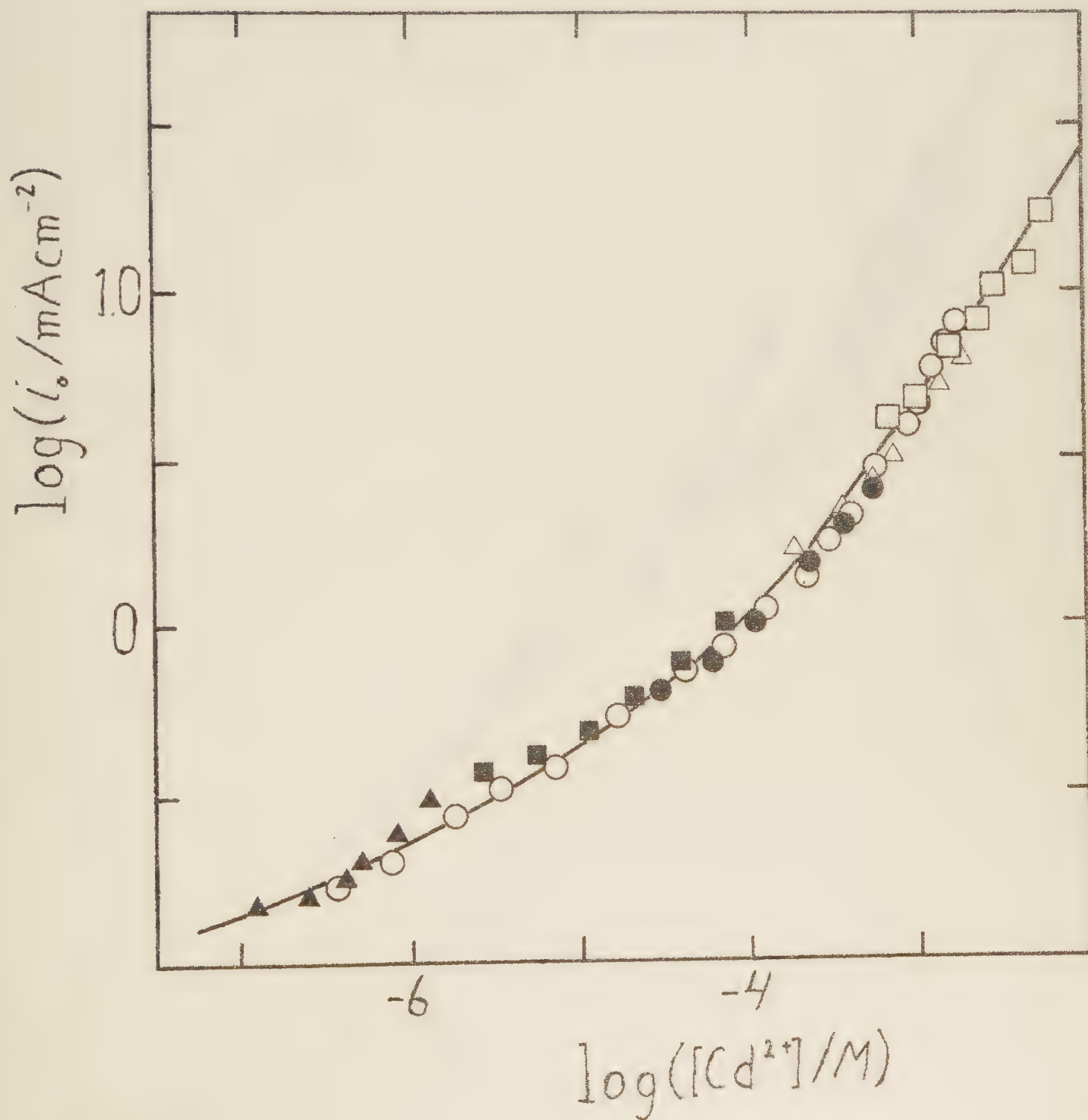


Fig. 2. $\log i_0$ as a function of $\log [\text{Cd}^{2+}]$ in the bromide system at a constant C_{Cd} or $[\text{Br}^-]$. The symbols refer to the values given in Table 2. The curves have been calculated from the values of $k_{0,1}$ and $k_{j,2}$ in Table 4.

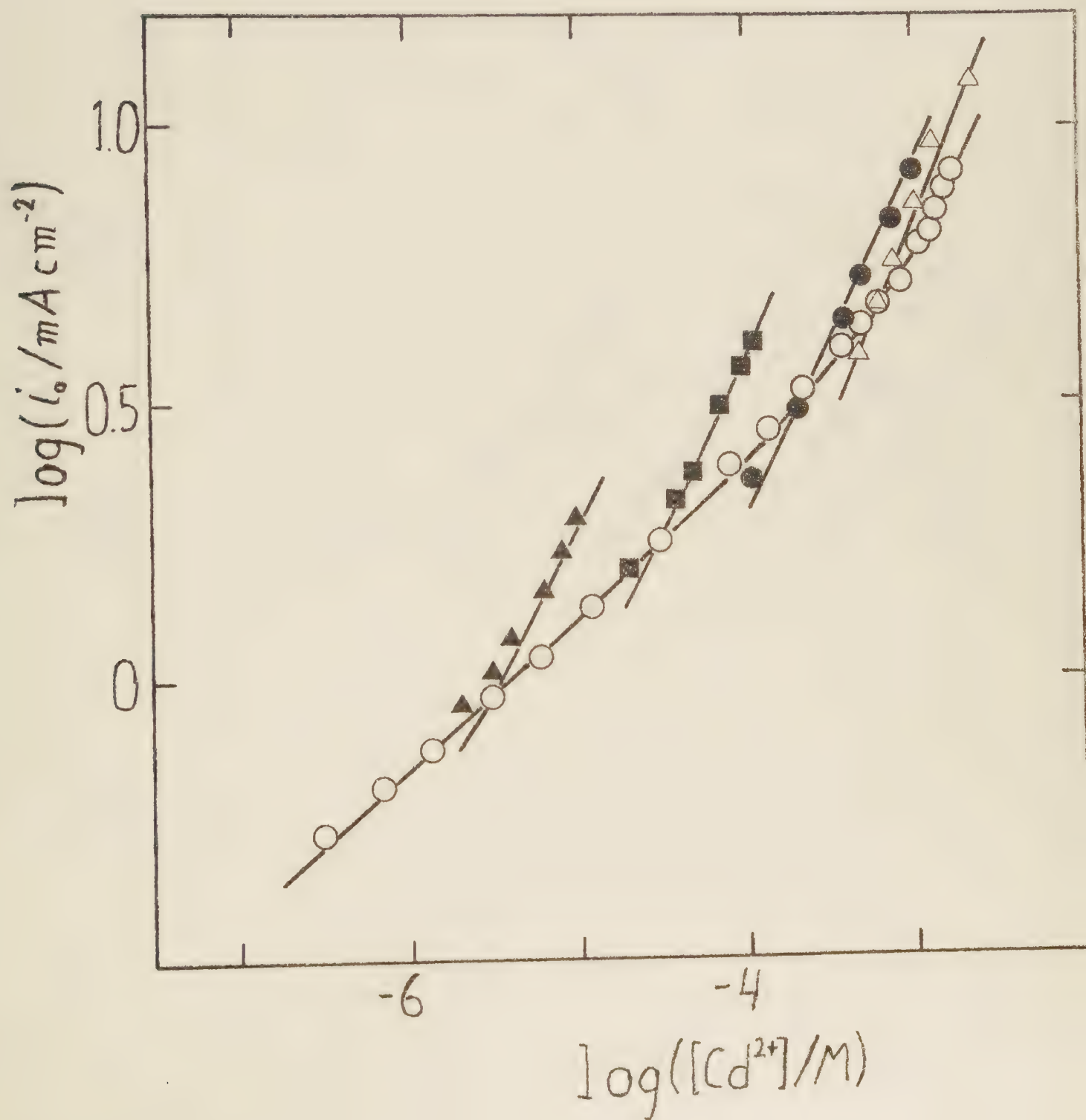


Fig. 3. $\log i_0$ as a function of $\log [\text{Cd}^{2+}]$ in the iodide system at a constant C_{Cd} or $[\text{I}^-]$. The symbols refer to the values given in Table 3. The curves have been calculated from the values of $k_{j,2}$ in Table 4.

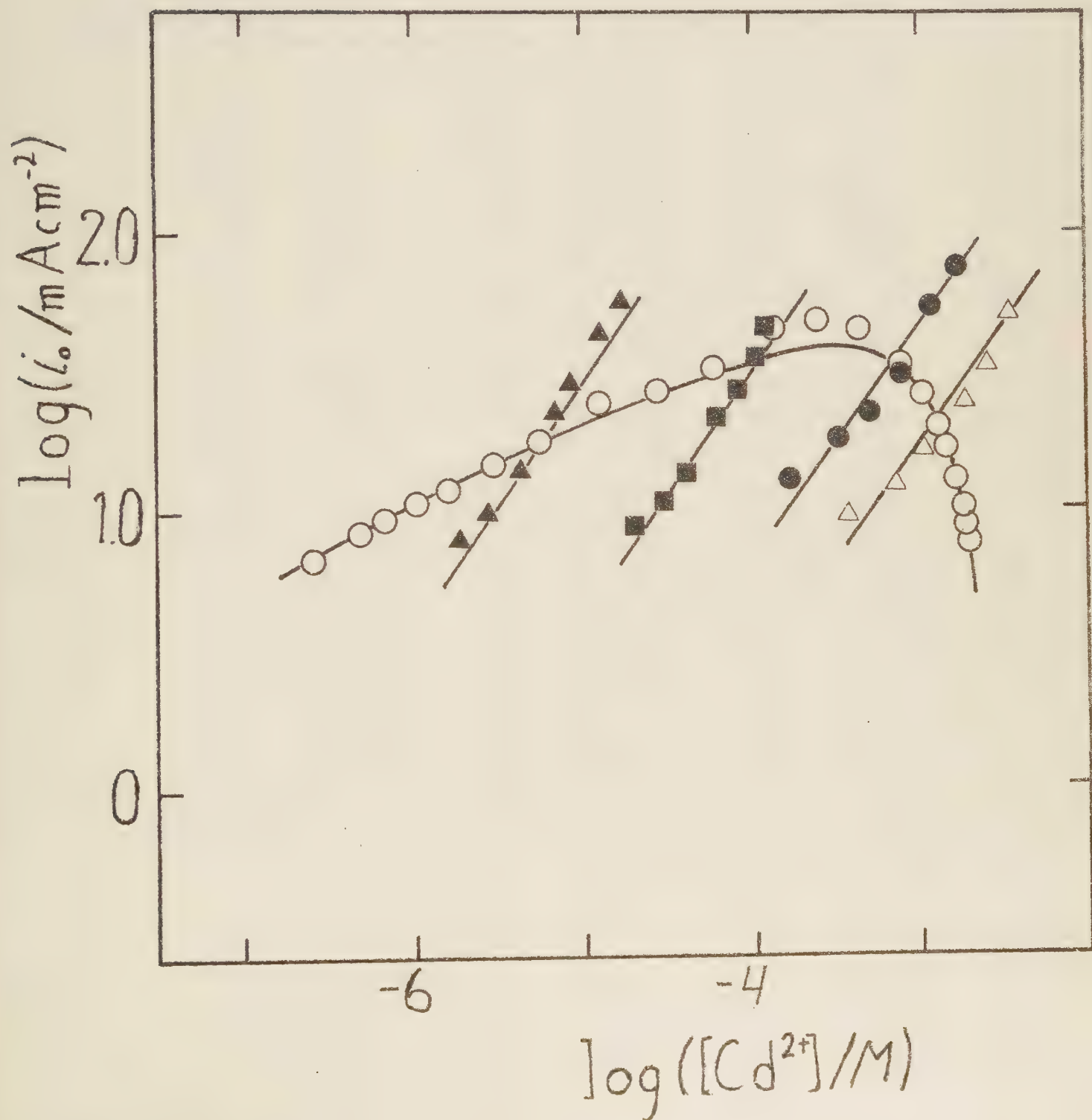


Table 1

Measurements of i_0 in the cadmium chloride system

$c_{\text{Cl}^-}/$ mM	$[\text{Cl}^-]/$ mM	$[\text{Cd}^{2+}]/$ mM	$i_0/$ mA cm^{-2}	$c_{\text{Cl}^-}/$ mM	$c_{\text{Cd}^{2+}}/$ mM	$[\text{Cd}^{2+}]$ mM	$i_0/$ mA cm^{-2}
$c_{\text{Cd}^{2+}}/\text{mM} = 2.00$ ○				$[\text{Cl}^-]/\text{mM} = 1.00$ △			
0.40	0.10	1.70	8.0	1.40	0.54	0.185	1.70
0.80	0.23	1.45	6.9	1.80	1.07	0.37	2.20
1.20	0.37	1.20	5.8	2.20	1.60	0.55	2.70
1.60	0.55	1.00	4.7	2.60	2.10	0.73	3.2
2.00	0.75	0.85	4.0	4.05	4.05	1.40	5.2
3.00	1.25	0.57	2.95	4.95	5.25	1.80	6.1
4.00	1.80	0.40	2.10	$[\text{Cl}^-]/\text{mM} = 4.00$ ●			
5.00	2.40	0.29	1.80	4.75	0.42	0.028	0.63
5.95	3.00	0.215	1.40	5.60	0.89	0.060	0.76
7.95	4.25	0.120	1.10	6.90	1.64	0.110	1.00
9.90	5.50	0.071	0.87	9.90	3.30	0.220	1.50
11.9	6.9	0.042	0.74	14.1	5.65	0.38	1.95
15.8	10.0	0.0155	0.54	18.3	8.05	0.54	2.50
19.6	13.4	6.6×10^{-3}	0.38	$[\text{Cl}^-]/\text{mM} = 10.0$ ■			
23.5	17.0	3.2×10^{-3}	0.33	11.0	0.34	2.7×10^{-3}	0.36
27.0	20.5	1.70×10^{-3}	0.27	11.9	0.68	5.4×10^{-3}	0.41
33.0	26.0	7.4×10^{-4}	0.20	13.8	1.32	0.0105	0.46
38.5	31.5	3.8×10^{-4}	0.170	17.5	2.65	0.021	0.60
$[\text{Cl}^-]/\text{mM} = 0$ □				24.0	4.90	0.039	0.76
				38.0	9.80	0.078	1.00
				$[\text{Cl}^-]/\text{mM} = 30.0$ ▲			
				32.0	0.58	1.30×10^{-4}	0.150
				34.1	1.16	2.6×10^{-4}	0.160
				36.2	1.74	3.9×10^{-4}	0.175
				38.1	2.30	5.2×10^{-4}	0.20
				43.3	3.75	8.4×10^{-4}	0.24
				50.5	5.80	1.30×10^{-3}	0.31

Table 2

Measurements of i_0 in the cadmium bromide system

$c_{\text{Br}^-}/$ mM	$[\text{Br}^-]/$ mM	$[\text{Cd}^{2+}]/$ mM	$i_0/$ mA cm^{-2}	$c_{\text{Br}^-}/$ mM	$c_{\text{Cd}^{2+}}/$ mM	$[\text{Cd}^{2+}]/$ mM	$i_0/$ mA cm^{-2}
$c_{\text{Cd}^{2+}}/\text{mM} = 2.00$ ○				$[\text{Br}^-]/\text{mM} = 2.00$ △			
0.40	0.15	1.75	8.4	3.50	1.50	0.46	3.9
0.80	0.35	1.55	7.7	4.00	2.00	0.61	4.8
1.20	0.50	1.40	7.1	4.45	2.50	0.76	5.7
1.60	0.70	1.25	6.5	5.20	3.25	1.00	7.3
2.00	0.90	1.10	6.2	5.85	3.90	1.20	9.6
2.95	1.40	0.83	5.3	9.25	7.35	2.25	11.9
4.00	1.95	0.63	4.8	$[\text{Br}^-]/\text{mM} = 4.00$ ●			
5.00	2.50	0.48	4.4	5.45	0.83	0.100	2.35
5.95	3.05	0.37	4.0	6.90	1.65	0.200	3.1
7.90	4.25	0.215	3.3	9.80	3.30	0.40	4.5
9.85	5.45	0.130	2.80	11.1	4.05	0.49	5.2
11.8	6.9	0.077	2.45	14.8	6.15	0.74	6.7
15.7	9.9	0.029	1.80	18.2	8.05	0.97	8.2
19.5	13.4	0.0115	1.35	$[\text{Br}^-]/\text{mM} = 10.0$ ■			
23.5	16.8	5.6×10^{-3}	1.10	13.8	1.33	0.0185	1.60
27.0	20.5	3.0×10^{-3}	0.93	17.5	2.65	0.037	2.10
32.5	26.0	1.30×10^{-3}	0.76	19.5	3.30	0.046	2.30
38.0	31.0	6.8×10^{-4}	0.64	24.0	4.90	0.068	3.1
46.0	39.0	3.1×10^{-4}	0.54	28.5	6.45	0.090	3.6
				33.0	7.95	0.110	4.0
				$[\text{Br}^-]/\text{mM} = 20.0$ ▲			
				24.1	1.21	1.90×10^{-3}	0.92
				26.0	1.80	2.85×10^{-3}	1.05
				28.0	2.40	3.8×10^{-3}	1.20
				33.0	3.90	6.1×10^{-3}	1.45
				36.0	4.80	7.5×10^{-3}	1.70
				40.0	5.90	9.3×10^{-3}	1.95

Table 3

Measurements of i_0 in the cadmium iodide system

$c_I /$ mM	$[I^-] /$ mM	$[Cd^{2+}] /$ mM	$i_0 /$ $mA\ cm^{-2}$	$c_I /$ mM	$c_{Cd} /$ mM	$[Cd^{2+}] /$ mM	$i_0 /$ $mA\ cm^{-2}$
$c_{Cd} / mM = 2.00$ ○				$[I^-] / mM = 3.00$ △			
0.40	0.30	1.90	8.0	3.30	0.57	0.36	10.0
0.80	0.65	1.80	9.2	3.55	1.13	0.72	12.5
1.40	1.10	1.70	10.5	3.80	1.65	1.05	16.5
2.00	1.60	1.60	13.5	4.45	2.85	1.80	25
2.95	2.30	1.40	17.0	5.00	3.95	2.5	34
4.00	3.00	1.25	20	5.75	5.50	3.5	50
5.95	4.25	1.00	27	$[I^-] / mM = 6.00$ ●			
7.90	5.55	0.79	34	6.60	0.46	0.165	13.5
11.8	8.25	0.44	45	7.15	0.92	0.33	18.0
15.7	11.2	0.240	50	7.75	1.40	0.50	23
19.5	14.3	0.130	45	8.90	2.30	0.83	32
25.0	19.5	0.057	33	10.0	3.20	1.15	55
31.0	24.5	0.028	27	11.8	4.60	1.65	75
38.0	32.0	0.0125	25	$[I^-] / mM = 15.0$ ■			
47.5	41.0	5.5×10^{-3}	17.5	15.9	0.34	0.0200	9.0
56.5	49.5	2.9×10^{-3}	15.0	16.4	0.52	0.030	11.0
65.0	58.5	1.65×10^{-3}	12.0	16.8	0.69	0.040	13.5
73.5	66.5	1.05×10^{-3}	10.5	17.7	1.03	0.060	22
82.0	75.0	6.9×10^{-4}	9.2	18.7	1.40	0.080	28
90.5	83.0	4.8×10^{-4}	8.4	19.5	1.70	0.100	35
106	99.0	2.6×10^{-4}	6.8	20.5	2.05	0.120	45
				$[I^-] / mM = 40.0$ ▲			
				42.0	0.60	1.80×10^{-3}	8.0
				43.0	0.90	2.70×10^{-3}	9.9
				45.0	1.50	4.5×10^{-3}	14.5
				47.5	2.25	6.7×10^{-3}	23
				49.5	2.95	8.8×10^{-3}	29
				54.5	4.35	0.0130	45
				59.5	5.85	0.0175	60

Table 4

Values obtained of the coefficients in eqns. (5) and (6) when $i_{0,1}$ and $i_{0,2}$ are expressed in mA cm^{-2} , and $[\text{Cd}^{2+}]$ and $[\text{X}^-]$ in M

Ligand	$k_{0,1}$	$k_{0,2}$	$k_{1,2}$	$k_{2,2}$
Cl^-	7.0 ± 0.4	$(2.8 \pm 0.2) \times 10^3$	$< 3 \times 10^4$	$< 1 \times 10^7$
Br^-	12 ± 2	$(2.9 \pm 0.2) \times 10^3$	$(2.0 \pm 0.4) \times 10^5$	$(1.0 \pm 0.1) \times 10^8$
I^-		$(2.8 \pm 0.2) \times 10^3$	$(1.6 \pm 0.1) \times 10^6$	$(5.6 \pm 0.4) \times 10^8$



Table 5

Components of charge and the ϕ_2 -potential in the electrode double-layer at the ionic strength 1 M and at the electrode potential -785 mV versus Ag, AgCl in 10 mM LiCl + 990 mM LiClO₄

Electrolyte	$-q/$ $\mu\text{C cm}^{-2}$	$F\Gamma_+ /$ $\mu\text{C cm}^{-2}$	$-\phi_2 /$ mV
20 mM LiCl } 980 mM LiClO ₄ }	7.9	5.2	39
1000 mM LiCl	8.1	5.4	40
500 mM LiBr } 500 mM LiClO ₄ }	8.0	5.2	39
1000 mM LiBr	8.0	5.6	41
1000 mM LiH · H ₂ O	7.0	6.3	45



Table 6

Ratios of the rate constants $k'_{j,2}$, relating to the charge transfer step $\text{Cd(II)}/\text{Cd(I)}$ in the bromide and iodide systems, and enthalpy changes, ΔH_j^0 , in the reactions $\text{CdX}_{j-1}^{3-j} + \text{X}^- \rightleftharpoons \text{CdX}_j^{2-j}$

Ligand	$k'_{1,2}/k'_{0,2}$	$k'_{2,2}/k'_{1,2}$	$\Delta H_1^0 /$ kJ mol^{-1}	$\Delta H_2^0 /$ kJ mol^{-1}
Cl^-	< 0.6		- 6.3	
Br^-	7	235	- 3.9	17
I^-	180	360	2.4	27
Ref			[8]	[8]

for the glycollate system imply that eqn. (9) is applicable whereas eqn. (10) is not. Furthermore, from this result it can be concluded that the disproportionation reaction (6) in this case is slow compared with the charge transfer steps.

Acetate¹² and pyruvate ions (paper II) have a very similar rate-enhancing effect on the electrode reaction (Fig. 2), and very probably the mechanism of the charge transfer is the same as that arrived at for the glycollate system. However, from Fig. 3 it is seen that $\bar{\alpha}$ is fairly constant in the pyruvate system and increases slowly with $[L^-]$ in the acetate system. These findings indicate that $Cu(II)/Cu(I)$ is the rate-determining step at all ligand concentrations used. This dissimilarity to the glycollate system can to some extent be explained by the weaker complex formation with $Cu(II)$, which makes the ratio $[Cu(I)]/[Cu(II)]$ decrease less than in the glycollate system.

The glyoxylate ion has the most pronounced catalytic effect on the electrode reaction. In this system there is a strong decrease in $\bar{\alpha}$ at increasing $[L^-]$, and $\bar{\alpha}$ becomes finally so low (≈ 0.3) that it must be concluded that $i_0 \sim i_{0,1}$ at these ligand concentrations. In paper II it has been shown that if this change of rate-determining step from $Cu(II)/Cu(I)$ to $Cu(I)/Cu(am)$ is explained in the same way as for the glycollate system by means of eqn. (9), a very high contribution to $i_{0,2}$ from the second complex CuL_2 must be presupposed. However, such an explanation is not very probable since it is found (see below) that the contribution from the first complex

CuL^+ is of the same magnitude as for the glycollate system.

Another and more probable explanation is that in the glyoxylate system as in the acetate and pyruvate systems $i_{0,1} \gg i_{0,2}$ within the whole ligand concentration range, but that at higher glyoxylate concentrations eqn. (10) could be valid instead of eqn. (9), yielding $i_0 \approx 0.5 i_{0,1}$. The application of eqn. (10) implies that the attainment of the disproportionation equilibrium (6) is speeded up very much by the formation of glyoxylate complexes, so that the two steps (3) and (4) become parallel instead of consecutive. As it is well-known that the glyoxylate ion as a bridging ligand has a remarkably strong rate-enhancing effect on certain homogeneous redox reactions^{13,35}, this ligand could have a similar catalyzing effect on the disproportionation reaction (6) for copper.

For the carboxylate solutions no electrocapillary measurements were carried out in this series of investigations, and thus no determination of the ϕ_2 -potential at the equilibrium electrode potential of the amalgam was possible. However, it is known from measurements of Payne³⁶ that the ϕ_2 -potential at mercury is negative in 1 M perchlorate solutions owing to specific adsorption of perchlorate ions. It has further been shown by Grahame and Soderberg³⁷ that acetate ions are only weakly specifically adsorbed, and this can be presupposed to be the case also with the other carboxylate ions used. Then, at the equilibrium potential of the amalgam the ϕ_2 -potential should be negative and have an approximately constant value for all the copper carboxylate solutions. Thus, the catalysis of the charge

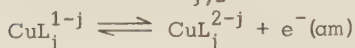
transfer Cu(II)/Cu(I) by the carboxylate ions cannot be explained by the Frumkin effect, as the average positive charge of the electro-active copper species and the attraction by the electrode double-layer decrease at the formation of complexes.

For a comparison between the effects of the different carboxylate ligands, the rate constants $k'_{0,2}$ and $k'_{1,2}$, relating to the participation of Cu^{2+} and CuL^+ , respectively, in the charge transfer step Cu(II)/Cu(I) , were calculated. The constants were obtained (I and II) from the relationship $i_0 = 2i_{0,2}$, valid at very low $[\text{L}^-]$ for all the carboxylate systems independently of any conclusions about the mechanisms at higher $[\text{L}^-]$. In the calculations the unknown stability constants of Cu(I) complexes CuL had to be replaced by the corresponding stability constants of the Ag(I) systems, which were known³³ or could easily be determined^{II}. It is very probable that the ratios of the $k'_{1,2}$ -values are but slightly influenced by this approximation.

Though no Frumkin corrections have been applied to the rate constants presented in Table 1, it is quite clear that the coordination of a carboxylate ion has a pronounced catalytic effect on the charge transfer Cu(II)/Cu(I) . It is also evident that the variation in $k'_{1,2}$ found with the different ligands cannot be correlated to the strength of the Cu(II) complexes or to the tendency of the ligands towards chelation.

On the other hand, it should be emphasized that the sequence of the carboxylate ions according to their catalytic effect, acetate < glycol-

Table 1.

Rate constants $k'_{j,2}$ relating to the charge transfer step

Ligand	$k'_{0,2}/\text{cm s}^{-1}$	$k'_{1,2}/\text{cm s}^{-1}$	β_1/M^{-1}
H ₂ O	0.10 ± 0.01		
CH ₃ COO ⁻		11	47 ± 1
HOCH ₂ COO ⁻		25	220 ± 10
HCOCOO ⁻		60	60 ± 3
CH ₃ COCOO ⁻		13	20 ± 1
Ref.	I, II		28, II

late<glyoxylate, is the same as that valid for the rate-enhancing effect of these ligands on certain homogeneous redox reactions¹³.

In the latter case, it was proved that the carboxylate group functions as an electron conducting bridge. Though the differences in catalytic effect between the different carboxylate ions are much smaller in the electrode reactions, the sequence found provides support for the suggestion that there is a weak but fast specific adsorption of copper complexes on the amalgam with the carboxylate group functioning as a bridge between the copper ion and the electrode, one oxygen atom being bonded to the amalgam surface and the other coordinated to the copper ion. Then the variations in $k'_{1,2}$ could be explained by differences in electron conducting ability of the bridging ligands or

possibly by differences in specific adsorbability of the complexes.

4.2 The zinc halide systems in DMSO

The kinetics of the electrode reactions of the zinc chloride, bromide and iodide systems in DMSO are presented in paper III. From impedance measurements on the chloride system it was found that the faradaic impedance has a "Randles behaviour". Thus, charge transfer and diffusion are rate-determining for the electrode reaction. This is also the case with zinc halide systems in water solutions³⁸. Furthermore, in DMSO solutions the faradaic impedance is dominated at the frequencies used by the charge transfer resistance.

For both the chloride and bromide systems it holds that $\log i_0$ plotted versus $\log [\text{Zn}^{2+}]$ can be represented approximately by a straight line, independent of if the total concentration, C_{Zn} , of Zn(II) in the solutions or the free halide concentration $[\text{L}^-]$ is chosen as the parameter. Thus, at a constant amalgam concentration a very simple expression

$$i_0 = k_0 [\text{Zn}^{2+}]^{\alpha_0} \quad (14)$$

is valid for the exchange current density. Here $[\text{Zn}^{2+}]$ has been calculated using the known stability constants. The exponent α_0 has the values 0.50 ± 0.03 and 0.60 ± 0.03 in the chloride and bromide systems, respectively. Also the values of k_0 found differ somewhat^{III}. It should be pointed out that the measurements on pure perchlorate solutions can be represented by the same expression as

that valid for the chloride system.

From a comparison between the relation experimentally arrived at and eqns. (2), (7) and (8) it can be concluded that at the ligand concentrations used the solvated zinc ions give a predominant contribution to i_0 , whereas the chloride and bromide complexes do not contribute noticeably, though already at low $[L^-]$ -values only a small fraction of C_{Zn} is present as non-complexed Zn^{2+} in the bulk of the solutions. There are two effects that can combine to make the participation of these complexes in the charge transfer not detectable. From the electrocapillary measurements (Table 2) at $E = -1175$ mV, that represents approximately the equilibrium potential of the zinc amalgam electrode, it can be calculated that the Frumkin correction, included as a factor in the composite coefficients k_j in eqn. (2), has a value of about 10^{1-j} and thus decreases rapidly with decreasing value of the net positive charge, $2-j$, of the complexes. In addition to this, the first complex is disfavoured in all the zinc halide systems³². Thus, at the ligand concentrations used in the kinetic measurements the ratio $[ZnL^+]/[Zn^{2+}]$ in the bulk of the solutions is always < 1 . A combination of the two effects mentioned should make the participation of the first chloride or bromide complex in the charge transfer undetectable in the absence of any catalysis.

The exponent 0.50 ± 0.03 for $[Zn^{2+}]$, found for the chloride system, makes it likely that in DMSO the charge transfer for the solvated Zn^{2+} is a two-electron transfer. Otherwise, if it is assumed that the charge transfer step Zn^{2+}/Zn^+ is rate-determining and that the

Table 2.

Components of charge and the ϕ_2 -potential in the electrode double-layer at the ionic strength 1 M and the electrode potentials -1175 mV and -785 mV versus Ag, AgCl in 10 mM LiCl + 990 mM LiClO₄ and with DMSO as solvent.

E = -1175 mV				E = -785 mV	
Electrolyte	$-q/$ $\mu\text{C cm}^{-2}$	$-q_1/$ $\mu\text{C cm}^{-2}$	$-\phi_2/$ mV	$-q/$ $\mu\text{C cm}^{-2}$	$-\phi_2/$ mV
20 mM LiCl 980 mM LiClO ₄ }	12.3	0.8	60	7.9	39
1000 mM LiCl	12.3	0.9	60	8.1	40
40 mM LiBr 960 mM LiClO ₄ }	12.2	1.6	62		
1000 mM LiBr	12.0	2.2	63	8.0	41
100 mM LiI · H ₂ O 900 mM LiClO ₄ }	12.5	2.0	64		
1000 mM LiI · H ₂ O	12.5	2.4	65	7.0	45
Ref.	III			IV	

equilibrium (6) is established, an unlikely low value ($\alpha_{0,2} \approx 0$) would be obtain for the anodic transfer coefficient, as in such a case the exponent for $[\text{Zn}^{2+}]$ would be $(1 + \alpha_{0,2})/2$ according to eqn.

(8). For water solutions the mechanism of the electrode reaction for the non-complexed Zn^{2+} is not yet known for certain (cf. refs. 18 and 39).

From the k_0 -value found with the chloride and perchlorate solutions and the ϕ_2 -value 60 mV (Table 2) a rate constant, k'_0 , corrected for the Frumkin effect, can be calculated^{III}. It has a value that is about 20 times lower than that valid in water solutions^{7,8}. Thus, the charge transfer process (1) for the solvated Zn^{2+} is a slower process with DMSO than with water as solvent. This is what could be expected, as it has been shown⁴⁰ that the solvation of Zn^{2+} is more exothermic in DMSO than in water.

With the iodide system it was found from $(\log i_0, \log [\text{Zn}^{2+}])$ -plots that i_0 is a function of both $[\text{Zn}^{2+}]$ and $[\text{I}^-]$. However, the quantity $\bar{\alpha}$, determined at different $[\text{I}^-]$, is constant and equal to 0.60 ± 0.03 , and the relation obtained for i_0 is of the following form.

$$i_0 = [\text{Zn}^{2+}]^{0.60} (k_0 + k_1[\text{I}^-]) \quad (15)$$

Here k_0 has the same value^{III} as in the bromide system. When this expression is compared with eqn. (2) it can be concluded that most probably both the solvated Zn^{2+} and the first complex ZnI^+ contribute to i_0 . The $[\text{I}^-]$ -term in eqn. (15) cannot be ascribed to an increase in $-\phi_2$ at increasing $[\text{I}^-]$, as it can be calculated from Table 2 that the variation in the Frumkin correction, included in k_0 , is only about 4 %, whereas the variation in $i_0/[\text{Zn}^{2+}]^{0.60}$ is about

25 %. A very plausible explanation of the contribution from ZnI^+ to i_0 is that there is a weak but fast specific adsorption of this complex on the amalgam surface, making the rate constant k_1' so high that the lower value of the Frumkin correction included in k_1 is more than compensated for.

Concerning the participation of the second and third complexes in the electrode reaction at the higher ligand concentrations used, when these complexes predominate in the solutions, it should be pointed out that it was not possible to determine low values of i_0 with high accuracy, and the Frumkin effect probably is sufficient to conceal the participation of these complexes, if no additional rate-enhancing effect is operative.

In the electrocapillary measurements it was found (Table 2) that in DMSO there is specific adsorption of the anions on mercury at $E = -1175$ mV. From the q_-^1 -values calculated it is evident that the specific adsorbabilities of Cl^- and ClO_4^- are very similar. Furthermore, the adsorbabilities of the halide ions increase in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$, but the variation is smaller than that found⁸ with water solutions of potassium halides. However, the adsorbability of I^- in DMSO is approximately the same as that determined previously⁴¹ for water solution. Thus, it can be concluded that the adsorbabilities of Cl^- and Br^- are stronger in DMSO than in water (cf. ref. 23). These findings are in agreement with the fact⁴² that Cl^- and Br^- are more weakly solvated in DMSO than in water, while the reverse holds for I^- .

It is quite clear from the results obtained that specific adsorption of the halide ions and complex formation, which exist in both DMSO and water, cannot explain separately why in DMSO the ratio $i_0/[Zn^{2+}]^{\alpha_0}$ is constant in Cl^- and Br^- -solutions but increases linearly and weakly at increasing $[I^-]$, whereas in water all of these halides make the corresponding quantity increase and the effect is very pronounced for I^- . Now, in DMSO the Cl^- and Br^- that are specifically adsorbed on the amalgam are surrounded by the larger DMSO molecules, which probably determine the distance of closest approach of the center of the solvated Zn^{2+} to the electrode. Thus, there should be a sort of steric hindrance to the coordination of Zn^{2+} to such an adsorbed anion. In other words, ligand bridging at the electrode by Cl^- or Br^- should not be possible. The larger and more polarizable I^- , on the other hand, could have a better possibility to act as an electron conducting ligand bridge. With water solutions no steric hindrance of this kind to ligand bridging can be expected for any of these halide ions.

In conclusion, the model of ligand bridging at the amalgam seems for the zinc halide systems to be the most practicable one in explaining the dissimilar results obtained from the kinetic measurements on water and DMSO solutions.

4.3 The cadmium halide systems in DMSO

The investigation on the electrode reactions of the cadmium chloride, bromide, and iodide systems in DMSO solutions is accounted for in

paper IV. For the chloride system it was found that all the kinetic measurements, performed at a constant cadmium(II) concentration or at a constant $[\text{Cl}^-]$, could be represented by a single $(\log i_0, \log [\text{Cd}^{2+}])$ -curve. Thus, i_0 is a function of $[\text{Cd}^{2+}]$ exclusively, and this means that at the chloride concentrations used the charge transfer is completely predominated by the solvated Cd^{2+} , whereas the participation of the chloride complexes is negligible. Consequently i_0 decreases rapidly on addition of Cl^- , while in water solution the charge transfer rate is enhanced¹⁸ in the presence of Cl^- . In this respect the system resembles the zinc chloride system, and the similar behaviour is what could be expected on the basis of the model of steric hindrance by DMSO molecules to ligand bridging at the electrode by Cl^- . The finding that in DMSO the chloride complexes do not contribute to i_0 is very important, as it made a study of the electrode reaction of the solvated Cd^{2+} possible down to $[\text{Cd}^{2+}] \approx 10^{-7} \text{ M}$.

The slope of the experimental curve showed that $\bar{\alpha}$ has a value of about 0.8 at the highest $[\text{Cd}^{2+}]$ used but then decreases gradually to about 0.25 at the lowest $[\text{Cd}^{2+}]$. This result indicates that the overall charge transfer cannot predominantly be a simple two-electron transfer but most probably proceeds as single-electron steps.

Furthermore, from the values $\bar{\alpha}$ it can be inferred that $i_0 \sim i_{0,2}$ at high $[\text{Cd}^{2+}]$, while $i_0 \sim i_{0,1}$ at low $[\text{Cd}^{2+}]$. It is easy to prove that this statement implies that eqn. (10) is applicable whereas eqn. (9) is not. Thus, there should be a fast disproportionation of the

intermediate Cd(I), making the two steps parallel instead of consecutive. Accordingly, all the measurements of i_0 can be represented very well by an expression of the form

$$i_0 = 0.5(k_{0,1}[\text{Cd}^{2+}]^{0.20} + k_{0,2}[\text{Cd}^{2+}]^{0.85}) \quad (16)$$

From eqn. (16) constant and reasonable anodic transfer coefficients, $\alpha_{0,1} = 0.40$ and $\alpha_{0,2} = 0.70$, of the two steps are obtained. The mechanism arrived at is similar to one proposed¹⁶ for water solutions.

An apparent rate constant, k'_0 , for the overall charge transfer of the solvated Cd^{2+} at high $[\text{Cd}^{2+}]$ can be calculated by using eqn. (2) and putting $\alpha_0 = 0.80$. It has a value that is about 50 times lower than that found with perchlorate solutions in water^{17,43}. Thus, the relative decrease in this rate constant at exchange of water for DMSO as solvent is of the same order of magnitude for Cd^{2+} and Zn^{2+} , and this result could be correlated to the fairly similar values⁴⁰, -68 and -60 kJmol^{-1} , of the enthalpies of transfer of these ions from water to DMSO.

The apparent cathodic transfer coefficient $1 - \alpha_0 (= 0.20)$ has about the same value as that determined¹⁷ for Cd^{2+} in perchlorate solutions in water as well as in various non-aqueous solvents. This resemblance could indicate one and the same mechanism of the charge transfer.

As to the nature of the intermediate it should be emphasized that a

dimeric Cd^{2+} , which has been discussed¹⁷ as a possibility in water solutions, would give a slope $\bar{\alpha} > 1$ at high $[\text{Cd}^{2+}]$. Consequently, such an intermediate is not possible in DMSO solutions, and Cd^+ seems to be the most probable intermediate.

Objections have previously¹⁷ been raised to a mechanism with Cd^+ in water solution as the intermediate. The reason was the very low value obtained in an estimate⁴⁴ of the standard potential of the $\text{Cd}^{2+}/\text{Cd}^+$ couple. However, in paper IV an estimate was performed, based on the reasonable assumptions that the free energy of hydration of Cd^+ can be put equal to that⁴⁵ of Ag^+ , as these ions should have fairly similar radii, and that the free energies of transfer of Cd^{2+} and Cd^+ from water to DMSO are approximately the same as those of Cu^{2+} and Cu^+ , respectively. With the resulting value of the equilibrium constant K of the disproportionation and the ϕ_2 -potential -40 mV, determined in electrocapillary measurements at $E = -785$ mV (Table 2), it could be calculated that $k'_{0,1} \approx k'_{0,2} \approx 1 \text{ cm s}^{-1}$.

Thus, the mechanism proposed does not give unreasonably high rate constants. Nevertheless, the fast disproportionation of Cd^+ is difficult to explain in terms of a bimolecular reaction in solution owing to the very low values of $[\text{Cd}^+]$ calculated. For this reason it is suggested that weakly solvated Cd^+ is stabilized by specific adsorption (cf. ref. 17) and that a fast disproportionation of adsorbed Cd^+ takes place on the amalgam surface.

Also in the bromide system i_0 decreases monotonically, at increasing

ligand concentrations, but in this case $(\log i_0, \log [\text{Cd}^{2+}])$ -plots show that i_0 is a function of both $[\text{Cd}^{2+}]$ and $[\text{Br}^-]$. All the measurements of i_0 can be represented very well by eqn. (16) with the addition of a $[\text{Br}^-]$ -term and a $[\text{Br}^-]^2$ -term according to eqn. (8). These results indicate that no bromide complexes seem to take part in the step $\text{Cd(I)}/\text{Cd(am)}$, while Cd^{2+} and most probably also the complexes CdBr^+ and CdBr_2 take part in the step $\text{Cd(II)}/\text{Cd(I)}$. As a result $i_{0,1}$ is of minor importance for i_0 in the whole measurements range. Since there is no indication that complexes of Cd(I) take part in the step $\text{Cd(I)}/\text{Cd(am)}$, it is assumed that the step $\text{Cd(II)}/\text{Cd(I)}$ should be formulated according to eqn. (5) instead of eqn. (4).

In the iodide system i_0 increases rapidly at a constant C_{Cd} and increasing $[\text{I}^-]$. Thus, there is a pronounced catalysis of the charge transfer on addition of iodide ions. Only at higher $[\text{I}^-]$, when anionic complexes predominate in the solutions, does i_0 decrease again. $(\log i_0, \log [\text{Cd}^{2+}])$ -plots show that also in this system i_0 is a function of both $[\text{Cd}^{2+}]$ and the ligand concentration. As $\bar{\alpha} \approx 0.85$ at all $[\text{I}^-]$ -values, it is evident that the term $i_{0,1}$ in eqn. (10) is negligible. In other respects the expression for i_0 found is quite analogous to that valid for the bromide system. Accordingly, it can be concluded that Cd^{2+} and especially CdI^+ and CdI_2 take part in the charge transfer $\text{Cd(II)}/\text{Cd(I)}$.

For a comparison between the different cadmium halide systems the ratios of the rate constants $k'_{j,2}$, relating to the participation of the

Table 3.

Ratios of the rate constants $k'_{j,2}$, relating to the charge transfer step Cd(II)/Cd(I) in the bromide and iodide systems and enthalpy changes, ΔH_j^0 , in the reactions $\text{CdL}_{j-1}^{3-j} + \text{L}^- \rightleftharpoons \text{CdL}_j^{2-j}$.

Ligand	$k'_{1,2}/k'_{0,2}$	$k'_{2,2}/k'_{1,2}$	$\Delta H_1^0/$ kJ mol^{-1}	$\Delta H_2^0/$ kJ mol^{-1}
Cl^-	< 0.6		-6.3	
Br^-	7	235	-3.9	17
I^-	180	360	2.4	27
Ref.	IV		7	

complex CdL_j^{2-j} in the charge transfer step Cd(II)/Cd(I) was calculated (Table 3). To retain the dimension length/time for the rate constants, when the charge transfer step is formulated according to eqn. (5), they have been defined somewhat differently (cf. IV) than for the copper carboxylate systems. The constants have also been corrected for the Frumkin effect to become comparable.

The values of $k'_{1,2}/k'_{0,2}$ lead to the conclusion that ligand bridging is not very probable in the bromide system but could very well be the cause of the pronounced catalysis of the charge transfer in the presence of I^- . The finding that $k'_{2,2}/k'_{1,2}$ has not very different values in the two systems makes it improbable that a double ligand bridge can be operative for the complex CdI_2 .

From a comparison between the zinc and cadmium iodide systems it is found that the influence on the charge transfer from the first complex is more striking in the cadmium system. This is what could be expected, since Cd^{2+} as a softer acceptor than Zn^{2+} has a larger partial covalent character of the bond to I^- , and consequently the catalytic effect of ligand bridging should be larger.

The high values of $k'_{2,2}/k'_{1,2}$ could be correlated to the fairly large and positive values (Table 3) of the enthalpy change, ΔH_2^0 , at the formation of the complexes CdBr_2 and CdI_2 in DMSO. These positive ΔH_2^0 have been interpreted²⁰ as indicating a change from octahedral to tetrahedral coordination at this step of the complex formation. Such a change in the inner sphere of solvation should diminish the difference in solvation between Cd(II) and Cd(I) and thus also lower the energy of activation of the charge transfer step $\text{Cd(II)}/\text{Cd(I)}$. Results from preliminary measurements⁴⁶ in this laboratory on the cadmium thiocyanate system are in accordance with the correlation proposed. It can be said about CdBr_2 and CdI_2 that they represent "more electroactive" complexes, and in this case a plausible explanation of their electrochemical behaviour has been given. All the results obtained support the suggestion that the rate constant of the step $\text{CdL}_j^{2-j}/\text{Cd(I)}$ depends upon both the possibility of ligand bridging at the amalgam and the enthalpy change at the reaction $\text{Cd}^{2+} + j\text{L}^- \rightleftharpoons \text{CdL}_j^{2-j}$.

Concerning the anionic complexes, which are the prevailing ones in the bulk of the solutions at the highest halide concentrations used,

it should be emphasized that no additional rate-increasing effect can be expected. In that case the Frumkin effect could be sufficient for making the participation of these complexes in the electrode reaction not detectable.

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6. REFERENCES

1. J. Heyrovský, *Discuss. Faraday Soc.*, 1 (1947) 212.
2. R. de Levie, *J. Electrochem. Soc.*, 118 (1971) 185 C.
3. D.A. Aikens and J.W. Ross, *J. Phys. Chem.*, 65 (1961) 1213.
4. D.J. Barclay, E. Passeron and F.C. Anson, *Inorg. Chem.*, 9 (1970) 1024.
5. L. Pospíšil and R. de Levie, *J. Electroanal. Chem.*, 25 (1970) 245.
6. L.G. Sillén and B. Liljeqvist, *Sven. Kem. Tidskr.*, 56 (1944) 85.
7. R. Tamamushi and N. Tanaka, *Z. Phys. Chem. N.F.*, 39 (1963) 117.
8. P. Teppema, M. Sluyters-Rehbach and J.H. Sluyters, *J. Electroanal. Chem.*, 16 (1968) 165.
9. M. Sluyters-Rehbach, J.S.M.C. Breukel and J.H. Sluyters, *J. Electroanal. Chem.*, 19 (1968) 85.
10. J. Blackledge and N.S. Hush, *J. Electroanal. Chem.*, 5 (1963) 435.
11. R. Johansson, *Acta Chem. Scand.*, 18 (1964) 1809.
12. S. Fronæus, R. Johansson and C.O. Östman, *Chem. Scr.*, 1 (1971) 52.
13. H. Taube and S. Gould, *Acc. Chem. Res.*, 2 (1969) 321.
14. S. Ahrlund and N.O. Björk, *Acta Chem. Scand.*, A30 (1976) 265.

15. J.O'M. Bockris in E. Yeager (Ed.), *Trans. Symp. Electrode Processes*, Philadelphia, 1959, Wiley, New York 1961, p. 325.
16. B. Lovreček and N. Marinčič, *Electrochim. Acta*, 11 (1966) 237.
17. T. Biegler, E.R. González and R. Parsons, *Collect. Czech. Chem. Commun.*, 36 (1971) 414.
18. F. van der Pol, M. Sluyters-Rehbach and J.H. Sluyters, *J. Electroanal. Chem.*, 58 (1975) 177.
19. H.P. van Leeuwen and J.H. Sluyters, *J. Electroanal. Chem.*, 39 (1972) 233.
20. S. Åhrland and N.O. Björk, *Acta Chem. Scand.*, A30 (1976) 249, 257.
21. S. Frøen and C.O. Östman, *Acta Chem. Scand.*, 8 (1954) 961.
22. B.E. Conway and J.O'M. Bockris, *Electrochim. Acta*, 3 (1961) 340.
23. S.H. Kim, T.N. Andersen and H. Eyring, *J. Phys. Chem.*, 74 (1970) 4555.
24. P. Delahay, *Double Layer and Electrode Kinetics*, Interscience, New York, 1965.
25. J.E.B. Randles, *Discuss. Faraday Soc.*, 1 (1947) 11.
26. B.V. Ershler, *Discuss. Faraday Soc.*, 1(1947) 269.
27. M.D. Wijnen and W.M. Smit, *Rec. Trav. Chim.*, 79 (1960) 22, 203.
28. L.A. Hansen and J.W. Williams, *J. Phys. Chem.*, 39 (1935) 439.

29. R.S. Hansen, D.J. Kelsh and D.H. Grantham, *J. Phys. Chem.*,
67 (1963) 2316.
30. D.C. Luehrs, R.T. Iwamoto and J. Kleinberg, *Inorg. Chem.*,
5 (1966) 201.
31. S. Fronæus, *Komplexsystem hos koppar*, Diss., University
of Lund, 1948.
32. S. Åhrland and N.O. Björk, *Coord. Chem. Rev.*, 16 (1975) 115.
33. A.A. Pilla, *J. Electrochem. Soc.*, 117 (1970) 467.
34. L.G. Sillén and A.E. Martell, *Stability Constants of Metal-
Ion Complexes*, The Chemical Society, London, 1964.
35. H.J. Price and H. Taube, *Inorg. Chem.*, 7 (1968) 1.
36. R. Payne, *J. Phys. Chem.*, 70 (1966) 204.
37. D.C. Grahame and B. A. Soderberg, *J. Chem. Phys.*, 22
(1954) 449.
38. J.E.B. Randles and K.W. Somerton, *Trans. Faraday Soc.*,
48 (1952) 951.
39. B. Timmer, M. Sluyters-Rehbach and J.H. Sluyters, *J. Electro-
anal. Chem.*, 14 (1967) 181.
40. S. Åhrland, L. Kullberg and R. Portanova, *Acta Chem. Scand.*,
to be published.
41. D.C. Grahame, *J. Am. Chem. Soc.*, 80 (1958) 4201.
42. C.V. Krishnan and H.L. Friedman, *J. Phys. Chem.*, 73 (1969)
3934.
43. G.C. Barker in E. Yeager (Ed.), *Trans. Symp. Electrode
Processes*, Philadelphia, 1959, Wiley, New York, 1961,
p. 325.

44. J.H. Baxendale and R.S. Dixon, Z. Phys. Chem. (Frankfurt),
43 (1964) 161.
45. R.M. Noyes, J. Am. Chem. Soc., 84 (1962) 513.
46. S. Fronæus and B. Palm, Acta Chem. Scand., to be published.

